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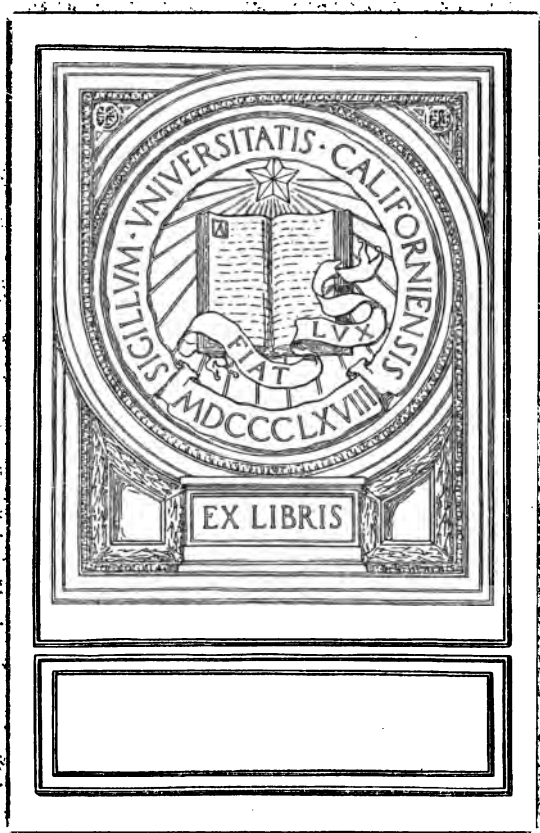
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HEAT FOR ENGINEERS.

A Treatise on Heat

*WITH SPECIAL REGARD TO ITS PRACTICAL
APPLICATIONS*

BY

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Associate of the Royal College of Science, Dublin; Whitworth Exhibitioner;
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PREFACE

TO

THE SECOND EDITION

THE author desires to express his thanks for the reception accorded to the first edition of this book, the disposal of which, in a comparatively short time, confirms his view that a treatise embodying the principles and practical applications of Heat would commend itself to engineers and to students of applied science. It has been a source of much satisfaction to learn that the contents have been found useful in many industrial establishments, in which the economic aspects of the subject are of great importance. The adoption of the treatise as a text-book in a number of educational institutions of high standing has been further gratifying to the author, who has long been of opinion that a presentation of the facts concerning Heat from a practical point of view would in all cases be preferable to the mere academic treatment of the subject.

In the present edition a number of errors which escaped detection in the first issue have been corrected, and paragraphs added where necessary summarizing the results of recent investigations bearing upon different branches of the subject. It is hoped that these alterations will be found to add to the value of the book.

CHAS. R. DARLING.

WOOLWICH : 1911.

P R E F A C E.

THE writing of this book was suggested to the author by DR. SILVANUS P. THOMPSON, F.R.S., Principal of the City and Guilds Technical College, Finsbury, at which Institution the author has for some years discharged the duties of Lecturer in Heat, and has also conducted laboratory studies in this subject. The practical applications of heat in the various branches of engineering are now so numerous and important that adequate treatment cannot be given to them in books devoted mainly to theory. Such subjects, for example, as Refrigerating Machinery, Ice Manufacture, Cold Storage, Fuels, and Pyrometry, although of great commercial importance, seldom receive more than the briefest mention in ordinary treatises on heat, and the engineer or student seeking information on these matters, frequently finds it difficult to obtain. The object of the present volume is to deal with the numerous applications of heat in modern industrial processes, and to furnish the information and data requisite for a correct understanding of the thermal phenomena involved.

The author has endeavoured throughout to explain thoroughly the principles underlying the matters dealt with, as mere technical descriptions, unaccompanied by such explanations, do not result in an intelligent grasp of the subject being obtained. The connection between heat and work has been kept prominent throughout; and the use of the various formulæ given has been illustrated by examples embodied in the text. Every care has been taken to include the most recent and reliable data in the numerous tables, and the recent advances in the science have, as far as possible, been given mention. A number of original experimental methods and commercial tests will be found in the book, based on the author's laboratory experience.

In order to keep the volume within the limits contemplated, the author has been compelled to exclude matter which, in the opinion of some, might, with advantage, have been included. The growth o

scientific knowledge in recent years is such as to make it possible to compile a treatise on almost every section of the subjects embraced in the present volume; and in selecting the matter for inclusion, the author has been largely guided by his own experience of the requirements of engineers and engineering students. In the chapters dealing with the conversion of heat into work, for example, the author has restricted himself to an explanation of the two fundamental laws of thermodynamics, and the consideration of the disposal of heat in actual engines in conjunction with these laws. In this, and other cases in which restriction has been necessary, the author has endeavoured to include sufficient to give the reader a grasp of the points of fundamental importance.

With regard to the question of units, the author has recognised the fact that British engineers—whether rightly or wrongly—do not favour the metric system of weights and measures, or the Centigrade scale of temperature; and accordingly the pound, foot, and Fahrenheit scale, figure frequently in the book. The term “calorie” is retained for the gram-degree Centigrade unit of heat, as the attempt to use this term to express a kilogram-degree Centigrade unit, with a view to replacement of the British Thermal Unit, has resulted in confusion only, and has not achieved the desired end.

The special thanks of the author are due to Dr. SILVANUS P. THOMPSON, F.R.S., for invaluable assistance in collecting materials for the various chapters, and for most useful advice during the writing of the book. To Mr. J. HUSBAND, of Sheffield University, the author also tenders his sincerest thanks for a number of excellent illustrations of practical appliances, and for many valuable suggestions. The author also wishes to acknowledge the kindness of numerous firms who have placed information and illustrations at his disposal.

CHAS. R. DARLING.

WOOLWICH: 1908.

HEAT FOR ENGINEERS.

CHAPTER I.

HEAT AS A FORM OF ENERGY. UNITS.

Heat as Energy.—Previous to the commencement of the nineteenth century, heat was generally regarded as being due to the action of a fluid which pervaded matter, to which the name “caloric” was given. This fluid was regarded as indestructible, and was further supposed to be self-repellent, although strongly attracted by the particles of matter. When a substance became warmer, it was held that “caloric” was added to it; and conversely was believed to grow colder owing to “caloric” leaving it. This theory, modified as occasion demanded, served to explain most of the known phenomena connected with heat.

The first experimental observations which resulted in establishing the modern view of the nature of heat were made by Count Rumford in 1798. Whilst engaged in the boring of brass cannon at Munich, Rumford was impressed by the great amount of heat developed in the operation. In order to investigate the matter quantitatively, he surrounded one end of the cannon by a wooden box, in which water was placed, and employed a blunt boring-tool, in order to remove as little brass as possible, and thus permit of the continuation of the experiment. By causing the cannon to revolve between the centres of a lathe, Rumford found that it was possible to boil the water; and moreover found that heat was produced in undiminished quantity so long as the friction between the tool and the revolving cannon was maintained. According to the caloric theory, the quantity of heat produced by such a method should be limited by the amount present in the bodies concerned; but Rumford's experiments showed that the supply was *inexhaustible*, and could only be rationally explained on the basis that work was convertible

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into heat continuously by the agency of friction. Rumford therefore expressed the view that "*heat is motion.*"

The supporters of the caloric theory, however, endeavoured to harmonise the results of Rumford's experiments with their own views, and some years elapsed before heat was generally recognised as a form of energy. The work of Dr. Joule, of Manchester, commenced in 1840, placed the issue beyond doubt. Joule showed that when heat is produced by friction, or other means, the amount of work done always bears a definite ratio to the amount of heat produced. The numerical connection, as determined by Joule (and signified by the letter "J"), was 772 foot-pounds per British Thermal Unit; or that 772 foot-pounds of work, if converted into heat, would raise the temperature of 1 pound of water by 1° Fahrenheit. More recent determinations, with better appliances, indicate the figure 778 foot-pounds as being the true mechanical equivalent of a British Thermal Unit.

The view that heat is merely a form of energy has received ample confirmation in later times. The doctrine of the Conservation of Energy, which states that all the different forms of energy, such as electricity, mechanical energy, heat, etc., are only modifications of one another, and may be converted into each other without the destruction of energy, is well exemplified in the transformations that heat may be made to undergo. Thus the heat from fuel burnt in the boiler of an engine is converted into work by the agency of steam; the work may be expended in driving a dynamo and producing electricity; and, by passing the electricity through a resistance, heat is again reproduced. Heat may be converted directly into electricity by means of a junction of two different metals, which, when heated, give rise to an electric current in a closed circuit. Hammering a substance, or rubbing one substance on another, gives rise to heat, and represents the conversion of work into heat. Moreover, whenever it is possible to measure the amounts of energy involved, it is invariably found that a given quantity of one kind of energy, when converted into another kind, always gives rise to the same quantity of the latter, no matter under what circumstances the change has been effected. Hence, it is possible to predict the maximum amount of heat that can be produced by a given amount of work, or the maximum number of units of electricity obtainable from a given quantity of heat or work.

Heat, as a form of energy, bears many resemblances to light, and in the form of radiant heat possesses the properties of light. All

bodies send off heat in the form of waves, and such heat waves possess not only the same velocity as light, but are capable of refraction, dispersion, reflection, and polarisation. The heat of the sun reaches the earth in the form of waves, and the sense of warmth experienced near a fire or hot substance arises from the same cause. It is due to this process of radiation (assisted by conduction and convection) that bodies at different temperatures in a room tend to attain the same temperature. The hotter bodies radiate more heat energy than they receive from the colder ones, and equilibrium is established when the heat radiated is balanced by the heat received.

The dissipation of all other forms of energy results in the production of heat. When the electricity disappears from a charged body, such as a rod of glass which has been rubbed, the disappearance is due to the conversion of the electricity into heat. Similarly, the result of stopping the motion of a projectile, in which mechanical energy disappears, is to produce an equivalent amount of heat. The general tendency of all kinds of energy, under the conditions obtaining on this planet, is to become heat. It is possible that under other conditions a converse tendency might be manifested, and speculations that all the energy in the universe will finally become "degraded" into heat should be received with caution.

Measurement of Heat and other forms of Energy: Units and Constants.—It is highly desirable, from the standpoint of the convertibility of the different forms of energy, that all units should be expressed in terms of common standards. Although this is carried out generally for scientific purposes, many of the units in everyday use have no accurate relation to each other. The British standards of weights and measures are wholly unsuited for the purpose of the calculations which enter daily into the duties of the engineer, and will no doubt ultimately be superseded or placed on a more scientific basis. For scientific work energy in all its forms is measured in terms of the centimetre, gram, and second—or, as abbreviated, C.G.S. units.

One centimetre = $\frac{1}{100}$ part of the standard of length in the metric system, viz. the metre.

One gram = the mass of 1 cubic centimetre of water at a temperature of 4° C.

The C.G.S. unit of *force* is 1 *dyne*, and is defined as "that force which, acting upon a mass of 1 gram for 1 second, generates a velocity of 1 centimetre per second.

The C.G.S. unit of *work* is 1 *erg*, and represents the amount of work done by 1 dyne acting through a distance of 1 centimetre.

The C.G.S. unit of *activity* or *rate of doing work* is 1 *erg* per second.

The above units are all "absolute" units, involving only the mass of 1 gram as distinct from a *weight* of 1 gram. The weight of 1 gram varies from place to place, whereas the quantity of matter it contains is constant. The weight of a substance depends upon the force with which gravitation acts upon it. For example, a lump of lead, if suspended on a delicate spring balance, would indicate a less weight at the equator than when near the poles, owing to the variation of the force of gravitation on the earth's surface. Any unit based upon the *weight* of a substance will therefore only have a fixed value in a given latitude, whereas "absolute" units are not subject to any such variation. Units in which "weight" is employed are termed "gravitation" units.

The C.G.S. "gravitation" unit of force is the weight of 1 gram, and at London is equal to 981 dynes, as a body falling *in vacuo* for 1 second has a velocity of 981 centimetres per second generated in it by gravitation. At other parts of the earth the acceleration produced by gravitation (*g*) differs from 981, and accordingly the unit of force expressed in terms of it would differ also. The same remarks apply to the other gravitation units, viz. the centimetre-gram, which is equal to 981 ergs in London, and the activity unit, which is 981 ergs per second, or 1 cm.-grm. per second.

The disadvantage of the C.G.S. units given above is that they involve very small quantities, and lead to large figures when employed for calculations on the large scale. It is therefore customary to employ larger units, consisting of multiples of the smaller units, when necessary. Thus the metre-gram = 100 cm.-grms. is sometimes employed; and also the metre-kilogram, which is equal to 100,000 cm.-grms. The activity unit, on the large scale, is the *force-de-cheval*, and is equal to 75 metre-kilos per sec. = 7,500,000 cm.-grms. per sec. = 7,360,000,000 or 7.36×10^9 ergs per second.

The practical unit of electrical work is the "joule," and represents 1 volt \times 1 ampère for 1 second. The choosing of the volt and ampère is such that 1 joule = 10,000,000 or 10^7 ergs. The rate of doing electrical work, or electrical activity unit, is the "watt," and is defined as 1 joule per second = 10^7 ergs per second. A larger unit, the kilowatt = 1000 watts, is frequently employed; and the Board of Trade unit, by which electricity is sold for consumption, is 1 kilowatt hour, or 1000 watts for 1 hour.

In British units the foot and pound take the place of the centimetre and gram in the C.G.S. units. The "absolute" unit of force is the *poundal*, and represents the force which, acting on a mass of 1 lb. for 1 second, generates a velocity of 1 foot per second. The unit corresponding to the erg is the *foot-poundal*, and is defined as the work done by a poundal working through a foot. The work-rate or activity unit is 1 foot-poundal per second. In practice the gravitation units are almost invariably employed. The foot-pound = 32.2 foot-poundals, as the value of g in the terms of the foot and second = 32.2 at London. A force of one pound = 32.2 poundals. The work-rate unit is 1 foot-pound per second. The larger work-rate unit = 550 ft.-lb. per second, or 33,000 ft.-lb. per minute, and is termed 1 horse-power. The numerical connection between the British and C.G.S. units will be found in the following table. Where the equivalent unit is represented by an excessively small fraction, it has been omitted.

Name of Unit	Equivalent in other Units					
	Centimetre-grams	Foot-lb.	Horse-power	Force-de-cheval	Watts	Ergs
Centimetre-gram	..	$\frac{1}{13,823}$	981 (London)
Foot-lb. .	13,823	$\{1.356 \times 10^7$ (London)
Horse-power	$\{7.6 \times 10^6$ per sec.	$\{33,000$ per min.	..	1.01385	746	$\{7.46 \times 10^9$ per sec.
Force-de-cheval	$\{7.5 \times 10^6$ per sec.	$\{32,549$ per min.	0.9863	..	736	$\{7.36 \times 10^9$ per sec.
Watt . .	$\{1.019 \times 10^4$ per sec.	$\{44.22$ per min.	$\frac{1}{746}$	$\frac{1}{736}$..	10^7 per sec.
Erg . .	$\frac{1}{981}$ (London)	$\frac{1}{1.356 \times 10^7}$	

Heat Units.—Although heat, as a form of energy, may be expressed in terms of energy units, such a mode of expression must be derived from some effect produced by heat on a standard substance. In terms of the centimetre and gram, the unit quantity of heat, or "*calorie*," is defined as the amount of heat required to raise the temperature of 1 gram of water by 1 degree Centigrade. In this definition no particular degree is specified, such as from 4° to 5°, or 40° to 41°, it being assumed that the amount of heat involved is the same whatever degree is selected. This is not the case, how-

ever, as less heat is required to raise the temperature of 1 gram of water 1° when the degree is chosen between 30° and 40° than at any other temperatures. The quantity involved at any temperature between 30° and 40° (e.g. 35° to 36°) is less than that required between 0° and 1° in the ratio 4173 to 4219, a difference which falls within the scope of many heat determinations. No special degree has yet been adopted, but the temperature rise of 17° C. to 18° C. is probably the best, and may finally come into general use. The heat required to raise 1 gram of water from 17° C. to 18° C. represents the average of that required for every degree between 0° and 100°; or $\frac{1}{100}$ part of the heat required to raise 1 gram of water from 0° to 100° C. In most ordinary heat calculations it is assumed that the gram-degree of heat is the same at all temperatures, and by choosing the degree 17 to 18 the least discrepancy would, in general, result from the assumption made. The variation of the calorie with temperature will only be taken into account in special cases in the examples given in succeeding chapters, in order to avoid confusion. It is highly desirable, however, that a standard degree should be adopted in connection with the unit, as a correction table could then easily be prepared and applied to a given result.

The disadvantage of the calorie as a practical unit is its smallness, large figures being involved when the heat values have reference to operations on the commercial scale. To overcome this drawback the *kilogram-degree Cent.* unit is sometimes employed. One of these units is equal to 1000 calories.

In engineering circles in Britain the unit generally adopted is the *British Thermal Unit* (B.Th.U.), which is defined as the amount of heat required to raise 1 lb. of water by 1 degree Fahrenheit. The interval represented by 1° F. is equal to $\frac{5}{9}$ of 1° C., and 1 lb. = 453·6 grams. The number of calories represented by 1 B.Th.U. will therefore be $453\cdot6 \times \frac{5}{9} = 252$.

In many cases, however, a heat unit involving the pound and degree Centigrade is used, and is known as the "*pound-degree Centigrade*" unit. It is evidently equal to 453·6 calories, and to $\frac{8}{5}$ or 1·8 British Thermal Units. Both these units are employed without reference to any specified degree of temperature. Adopting the temperature range recommended in the case of the calorie—17° C. to 18° C.—the corresponding interval on the Fahrenheit scale would be from 63° F. to 64° F. In practice the variation of the unit with temperature is seldom taken into account.

Energy Equivalents of Heat Units.—Expressed in ergs, the value of the gram-degree or calorie is represented by the round

number 42,000,000, or 4.2×10^7 . The energy equivalent of the *average* calorie, represented by 1 gram of water raised from 17° C. to 18° C., is 41,860,000, or 4.186×10^7 ergs. If the calorie be defined with respect to the range 0° C. to 1° C., the equivalent is 42,180,000 or 4.218×10^7 ergs. It will suffice for general purposes to use the round number 42,000,000 ergs as the equivalent of 1 calorie. This figure, multiplied by 252 and 453.6 respectively, will give the number of ergs represented by a B.Th.U. and a lb.-°C. unit. If expressed in centimetre-grams ($= \frac{\text{ergs}}{981}$) the value of the calorie is 42,650.

When the foot-pound is adopted as the work-unit, 1 calorie is represented by 3.087 ft.-lb.; 1 B.Th.U. by 778 ft.-lb.; and 1 pound-degree Centigrade unit by 1400 ft.-lb. The kilogram-degree Centigrade unit = 1000 calories, is equal to 3087 ft.-lb. One horse-power is equal to 23.57 lb.-°C. units, or 42.42 B.Th.U. per minute. A table showing the connections between the various heat units and the work values of each is appended for convenience of reference.

Unit	Equivalent in other Heat Units				Work Equivalent	
	Calories	Kilogram-degree Centigrade Units	British Thermal Units	lb.-°C. Units	Foot-lb.	Ergs
Calorie	$\frac{1}{1000}$	$\frac{1}{252}$	$\frac{1}{453.6}$	3.087	4.2×10^7
Kilogram-degree Centigrade	1000	..	3.97	2.205	3087	4.2×10^{10}
British thermal	252	.252	..	$\frac{5}{9}$	778	1.058×10^{10}
Pound-degree Centigrade	453.6	.4536	1.8	..	1400	1.905×10^{10}

The following data will be found useful for reference in calculations concerning heat :—

METRIC UNITS IN COMMON USE.

Length.

1 metre	= 39.37 inches.
1 centimetre	= .01 metre = .3937 inch.
1 millimetre	= .001 metre = .03937 „
1 kilometre	= 1000 metres = 3280.8 feet

Volume.

1 litre	= 1.762 pints	= 61.02 cubic inches.
1 cubic centimetre	} = .001 litre	= .06102 cubic inch.

Weight.

1 gram	= 15.432 grains.
1 milligram	= .001 gram.
1 kilogram	= 1000 grams = 2.2046 lb.

METRIC EQUIVALENTS OF BRITISH UNITS.

Length.

1 inch	= 2.54 centimetres.
1 foot	= 30.4801 "
1 yard	= 91.4404 "
1 mile	= 160,935 "

Volume.

1 cubic inch	= 16.388 cubic centimetres.
1 " foot	= 28.317 " "
1 pint	= 567.63 " "
1 gallon	= 4541.02 " "

Weight.

1 grain	= .0648 gram.
1 ounce avoird.	= 28.3495 grams.
1 lb.	= 453.59 "

Stress.

1 lb. per sq. inch	= 70.31 grams per sq. centimetre.
1 inch of mercury at 0° C.	} = 34.534 " "
30 inches of mercury at 0° C.	
1 centimetre of mercury at 0° C.	} = 13.596 " "
76 centimetres of mercury at 0° C.	
	= 1033.3 " "

Work and Energy.

1 foot-pound	{ = 13,823 centimetre-grams = 1.3560 × 10 ⁷ ergs.
1 foot-ton	
	{ = 3.096 × 10 ⁷ centimetre-grams = 3.0374 × 10 ¹⁰ ergs.

Work-rate.

$$1 \text{ horse-power} \quad \left\{ \begin{array}{l} = 7.604 \times 10^6 \text{ cm.-grms. per sec.} \\ = 7.46 \times 10^9 \text{ ergs per sec.} \end{array} \right.$$

MISCELLANEOUS DATA.

Specific gravity of mercury = 13.596 at 0° C.

Weight of 1 cubic inch of }
mercury } = .49125 lb.

Standard height of barometer = 76 centimetres = 29.92 inches.

Normal atmospheric pres- }
sure } = 1033.3 grams per sq. centi-
metre = 14.7 lb. per sq. in.

Weight of 1 litre of air at }
0° C. and 76 cm. pressure } = 1.293 grams.

Value of "g" at London }
} = 981.17 cm. per sec. = 32.2
feet per sec.

Weight of 1 cub. ft. of air at }
0° C. and 760 mm. press. } = .0807 lb.

Weight of 1 litre of }
hydrogen at 0° C. and }
760 mm. press. } = .0896 gram.

CHAPTER II.

METHODS OF PRODUCING HEAT. THE PROPERTIES, USES, AND
EVALUATION OF FUELS.

Methods of Producing Heat.—Heat energy may be produced in the following ways :—

1. Chemical action, such as the burning of coal or other matter in air or oxygen; the decomposition of an explosive; or the combination of quicklime with water.

2. By passing a current of electricity through a resistance, as in the case of incandescent, Nernst, or arc lamps. The dissipation of a charge of static electricity also gives rise to heat.

3. By friction. Bearings, when insufficiently lubricated, become hot owing to the production of heat by friction.

4. By percussion. The hammering of a piece of metal causes a rise of temperature; and a leaden bullet, on being brought to rest by striking a target, may be melted by the heat produced.

5. By the compression of a gas. A mixture of a combustible gas and air may be raised to the temperature of ignition by compression, as in certain forms of engines.

6. By the absorption of a gas by a porous solid. Freshly-made charcoal, if powdered, may become so hot from this cause as to ignite in air; and the heating of platinum caused by the absorption of hydrogen or coal gas is sufficient to ignite a jet of these gases.

7. By molecular re-arrangement. A bar of iron, cooling from a high temperature, suddenly becomes hotter again at certain stages, owing to molecular changes taking place which liberate energy in the form of heat.

8. By atomic decomposition, as illustrated in the case of radium compounds. The breaking up of the atoms sets free a considerable amount of energy in the form of heat.

Only the first two methods are of general importance in connection with the generation of heat on the large scale.

In producing heat for practical purposes, such as for furnaces or steam-raising, bodies known as *fuels* are employed. In general, the

heat is produced by the chemical union of carbon and hydrogen, which are contained in the fuel, with the oxygen of the air. Coal, coke and wood represent solid fuels; petroleum and its extracts, and also alcohol and certain hydrocarbons, such as benzol and naphthalene, are used as liquid fuels; whilst coal gas, natural gas and producer gas are employed as gaseous fuels. The selection of a fuel for a given purpose is guided by considerations of economy, suitability, and convenience.

In recent years great progress has been made in the utilisation of electricity for producing heat. Wherever fuel can be obtained at a reasonable price the cost of electrical heating will be the greater; but, on the other hand, a much higher temperature may be obtained by the aid of electricity. A number of electric furnace products, which are now in everyday use, cannot be obtained in furnaces employing fuel. Examples of these products are calcium carbide, used for making acetylene, and highly refractory substances such as carborundum, siloxicon, etc., used as furnace linings. Electric furnaces have the further advantages of easy control and localisation of heat, and will no doubt be extensively used in the future, particularly where cheap water-power is available.

Heating Power of Fuels.—The combustible portions of all fuels consist of one or more of the following:—

1. Free carbon.
2. Free hydrogen.
3. Carbon combined with one or more of the elements hydrogen, oxygen and nitrogen.

Experiments show that 1 gram of carbon, burning in air or oxygen, gives out 8080 calories. One lb. would therefore produce 8080 lb.-°C. units, or 14,544 B.Th.U. These figures represent the heat units given out when the carbon is completely converted into carbon dioxide (CO_2). If burnt so as to produce carbon monoxide (CO), the heat produced is much less, being 2420 calories per gram = 2420 lb.-°C. units per lb. = 4356 B.Th.U. per lb. When fuel is burnt in an insufficient supply of air, considerable quantities of carbon monoxide are formed, with the result that only a portion of the full heating power of the fuel is utilised. Hence the necessity for a sufficient amount of air if the best results are to be obtained.

The heat produced by the burning of 1 gram of hydrogen is 34,000 calories. One lb. will yield 34,000 lb.-°C. units, or 61,200 B.Th.U. Expressed as volume, 1 litre of hydrogen yields 3,046 calories (since 1 litre of hydrogen weighs 0.0896 gram), and 1 cubic foot will produce 191 lb.-°C. units, or 344 B.Th.U.

Compounds of carbon and hydrogen, when completely burnt in oxygen, produce carbon dioxide and water. The hydrocarbons commonly present in gaseous fuels are marsh gas or methane (CH_4) and olefiant gas or ethylene (C_2H_4). Liquid fuels consist of a mixture of many hydrocarbons, and in the burning of many kinds of coal numerous hydrocarbons are present in the flame. All these compounds, when burnt in excess of air, give rise to carbon dioxide and water. Alcohol contains oxygen, and has the formula $\text{C}_2\text{H}_6\text{O}$; the products of burning in this case also are carbon dioxide and water. The nitrogen present in fuels usually appears uncombined in the products; in some instances, however, it undergoes partial oxidation. This gas is never present to any great extent in solid or liquid fuels, but may form a large proportion of gaseous fuels, in which case it acts as an inert constituent.

The heating power of carbon compounds cannot be calculated from that of the constituents, but must be made the subject of direct experiment. Marsh gas, for example, contains 12 grams of carbon and 4 grams of hydrogen in 16 grams of the gas. Considered as free carbon and free hydrogen the heating power would be as under:—

$$\begin{array}{rcl}
 12 \times 8080 & = & 96,960 \text{ calories produced by 12 grams of carbon} \\
 34,000 \times 4 & = & 136,000 \quad \quad \quad \text{,,} \quad \quad \quad \text{,,} \quad \quad \quad 4 \text{ ,, hydrogen} \\
 \text{Total} & = & 232,960 \text{ calories}
 \end{array}$$

But experiment shows that 12 grams of carbon when *combined* with 4 grams of hydrogen form marsh gas: that is, 16 grams of marsh gas yield on burning only 209,600 calories. The difference between the two figures, viz. 23,360 calories, represents heat already evolved from the carbon and hydrogen in the act of combination.

Acetylene (C_2H_2) furnishes a further example of the thermal difference between a compound and its components in the free state, as the following figures show:—

26 grams of acetylene contain 24 grams of carbon and 2 grams of hydrogen.		
24 grams of carbon on burning in oxygen give		Calories. 193,920
2 , hydrogen ,, ,, ,,		68,000
Total		261,920

But 26 grams of acetylene on burning in oxygen give 294,000 calories, or 32,080 calories *more* than the free constituents.

In this case the chemical union of carbon and hydrogen to form acetylene is attended by the absorption of extraneous heat, which is liberated when the acetylene is burnt in oxygen or otherwise decomposed. Bodies which, like acetylene, absorb extraneous heat when forming are said to be "*endothermic*," whilst those which evolve heat during formation, such as water, carbon dioxide, and marsh gas, are termed "*exothermic*." The enormous energy developed by explosive compounds of the type of guncotton and nitro-glycerine is due to the liberation of heat absorbed during the formation of these substances, which are therefore, like acetylene, endothermic compounds.

The experimental determinations of the heating values of several compounds containing carbon and hydrogen is given in the following table :—

Substance		Calories per gram	Calories per litre	B.Th.U. per lb.	B.Th.U. per cubic foot
Gases	Marsh gas, CH_4 .	13,100	9,395	23,560	1052
	Ethylene, C_2H_4 .	11,900	14,910	21,420	1677
	Ethane, C_2H_6 .	12,350	16,610	22,230	1865
Liquids	Benzene, C_6H_6 .	10,100	9,090,000	18,180	..
	Alcohol, $\text{C}_2\text{H}_5\text{O}$.	6,900	5,457,900	12,420	..
	Petroleum (average) .	11,000	9,900,000	19,800	..
Solid	Naphthalene, C_{10}H_8 .	9,690	..	17,442	..

When the proportions of the mixture of combustible gases in a gaseous fuel are known by chemical analysis, it is possible to calculate the heating value of the fuel by assigning to each constituent its calorific value. In general, however, it is much simpler to find the heating value by direct experiment, as an exact chemical analysis of a mixture of gases is a somewhat tedious operation. In the case of solid and liquid fuels, analysis does not reveal the manner in which the hydrogen and oxygen are combined with the carbon, and consequently the heating value cannot be calculated with any degree of accuracy from analytical data, which merely furnish the percentage of each element present. In the case of coal, various formulæ have been proposed by means of which the calorific value may be approximately calculated from the constituents. Mahler's formula takes the form

$$Q = \frac{1}{100} [8140 C + 34,500 H - 3000 (O + N)]$$

where Q = calorific value in calories per gram, and C, H, O and N represent the percentages of carbon, hydrogen, oxygen and nitrogen respectively. The use of this formula in certain cases gives results not varying greatly from those found by direct experiment. Instances are known, however, in which specimens of coal, whilst possessing the same percentage composition, differ considerably in calorific value, and consequently no formula of this type can have any general application. An experimental determination is not only the simplest, but also the only reliable method of arriving at the heating value of a solid or liquid fuel. Instruments for this purpose are known as *fuel calorimeters*, and consist of three chief types, examples of which will now be described.

Fuel Calorimeters.—In all fuel calorimeters the method adopted is to burn a weighed quantity of the fuel in oxygen, so as to impart the heat produced to a known quantity of water. The number of heat units evolved is obtained by noting the rise of temperature produced in the water. The many varieties of instruments in use differ in the method of carrying out the combustion of the fuel, and also in the arrangements for imparting the heat to the water. All may be referred to one or other of the three following types:—

1. Calorimeters in which the fuel is burnt in oxygen under pressure. (Berthelot, modified by Mahler, Kroeker, Donkin, and others.)

2. Calorimeters designed for burning the fuel in a stream of air or oxygen. (W. Thomson, Junker, Wedmore, Darling, and others.)

3. Calorimeters in which a solid, such as potassium chlorate, sodium peroxide, or potassium nitrate, is mixed with the fuel to furnish oxygen for the combustion. (Lewis Thompson and others.)

Examples of each class of calorimeter will now be described, the instruments chosen in each case being suitable for commercial purposes.

Mahler's Calorimeter.—This instrument is a modification of the original "bomb" calorimeter of Berthelot, which was composed largely of platinum, and therefore very costly. The combustion of the fuel is carried out in a steel chamber (B, Fig. 1), enamelled on the interior to prevent oxidation or corrosion. A weighed quantity of the fuel is placed in a capsule C, preferably made of platinum, and may be ignited by passing a current of electricity through the fine iron or platinum wire F, which is embedded in the sample. The circuit through F is made by means of the rod E, which is insulated from the lid of the vessel B, and the corresponding rod which sustains the capsule. The chamber B is furnished with a

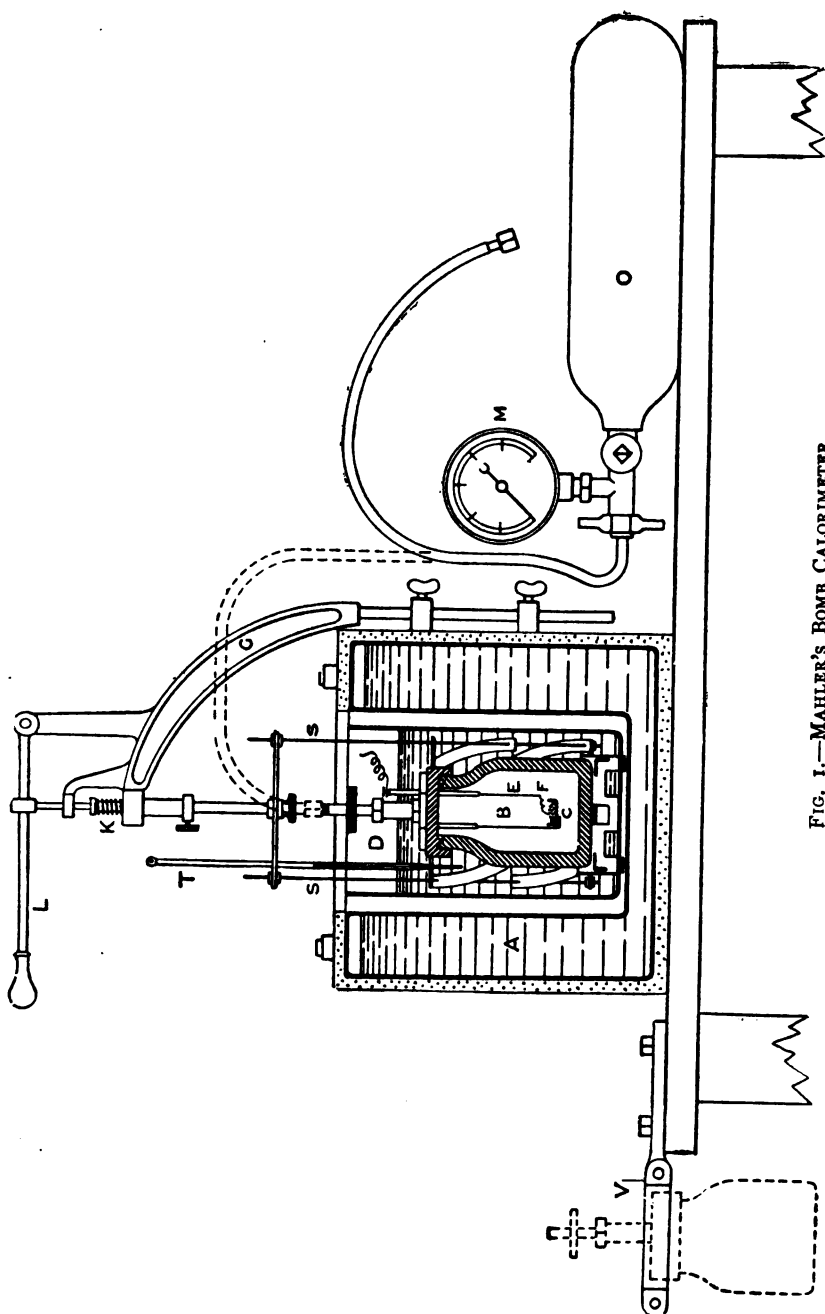


FIG. 1.—MAHLER'S BOMB CALORIMETER.

screwed top, and a valve for admitting oxygen from a cylinder. During the combustion the chamber B is surrounded by a known quantity of water in the vessel D, which stands on wooden supports in the double-walled shield A. The vessel A is encased in felt, and serves to protect D and its contents from external heat disturbances. The water in D is stirred by the arrangement S, which is caused to move up and down and also to rotate by means of the lever L, and the steep-pitched screw K. The rise in temperature is registered by the thermometer T.

In experiments with solid or liquid fuels 1 gram is placed in the capsule, and oxygen admitted to the combustion chamber until the pressure rises to 25 atmospheres. The capacity of the vessel D is such that 2200 grams of water are required in order that the combustion chamber may be completely immersed. The temperature of the water in D is noted, and the combustion started by passing a current of electricity through the wire F. As the combustion proceeds, the thermometer will show a gradual rise in temperature, and the experiment must be continued, with constant stirring, until the reading of the thermometer is stationary. The number of heat units developed is obtained by multiplying the weight of water taken in D by the rise in temperature, and adding to the result the number of heat units absorbed by the combustion chamber B, the vessel D, and the stirrer S, which also participate in the rise of temperature.

The capacity for heat possessed by the various parts of the apparatus is determined by a special experiment, and is recorded, for convenience of calculation, in terms of the amount of water which would absorb an identical quantity of heat; that is, the "*water equivalent*." To obtain this value a substance of known calorific power is burnt in the apparatus under experimental conditions, and the water equivalent calculated from the observed rise of temperature.

Example.—To find the water equivalent of a Mahler calorimeter, 1 gram of naphthalene was burnt under experimental conditions. Weight of water in vessel = 2200 grams; observed rise in temperature = 3.62°C. ; calorific value of naphthalene = 9690 calories per gram.

$$\begin{array}{ll} \text{Calories absorbed by water} & = (2200 \times 3.62) = 7964 \\ \text{"} & \text{"} \quad \text{apparatus} = (9690 - 7964) = 1726 \end{array}$$

Weight of water which would absorb 1726 calories on being raised through $3.62^{\circ}\text{C.} = \frac{1726}{3.62} = 476.8 \text{ grams.}$

The water equivalent was therefore 476.8 grams; that is, the heat taken up by the apparatus is equal to the quantity absorbed by 476.8 grams of water.

When the water equivalent has been accurately determined, it may be used in subsequent calculations by adding the figure to the actual amount of water taken, and multiplying the sum by the rise in temperature. The total number of heat units given out by the weighed sample of fuel is then obtained. Thus, if 1 gram of coal were burnt, and caused a rise of temperature of 3.2°C . in 2200 grams of water, the water equivalent of the apparatus being 480 grams, then the calorific value of the fuel would be $(2200 + 480) \times 3.2 = 8576$ calories per gram.

The heat developed by a gaseous fuel is obtained by exploding a known volume of the gas with an excess of oxygen in the combustion chamber. In this case the pressure before explosion should not exceed 5 atmospheres, as otherwise the force of the explosion might cause some of the joints to burst, and thus allow the hot gases to escape. The calculation is made as in the case of solid or liquid fuels.

In order to secure very exact results, the thermometer used is graduated so as to read to $\frac{1}{10}^{\circ}$ or $\frac{1}{100}^{\circ}\text{C}$.; and a correction for loss or gain of heat by radiation must be made. Results of extreme accuracy, however, are of more importance from the scientific rather than the commercial standpoint, for reasons that will be given later.

Other Varieties of "Bomb" Calorimeters.—Bryan Donkin's calorimeter resembles Mahler's in general arrangement and method of working, but the combustion chamber is gilt instead of enamelled. There are also slight differences in some of the minor details. In the form due to Kroecker, the lid of the combustion chamber is fitted with an arrangement whereby, on opening a valve, the remaining gases may be allowed to escape through a series of drying-tubes, by means of which the amount of water formed by the combustion may be determined. Other modified forms have been introduced by Hempel, Atwater, and others.

Carpenter's calorimeter occupies a position intermediate between the "bomb" type and those in which a stream of oxygen is used. In this calorimeter the combustion chamber is connected to a spiral of copper tubing, which is also surrounded by water. The oxygen is fed continuously into the chamber, and passes, together with the products of combustion, through the copper spiral, which terminate in a pin-hole outlet outside the combustion vessel. The excess of pressure over atmospheric is 2 to 5 lb. per square inch in the combus-

C

tion chamber. A feature of Carpenter's calorimeter is that the water in the vessel is completely closed in, and by expanding on heating rises up a graduated glass tube which passes into the vessel. The amount of the expansion observed furnishes the calorific power, the instrument having previously been standardised by burning substances of known calorific value. This apparatus does not furnish results as accurate as those of the bomb calorimeters; nor is complete combustion always obtained.

Commercial Uses of Bomb Calorimeters.—For ordinary commercial purposes, bomb calorimeters possess several drawbacks, notably the high cost, and the great care and skill necessary to work the apparatus. In Mahler's calorimeter, and others of the same type, there is no means of telling whether the ignition has been successful, other than the rise of temperature. A further drawback is the quantity of oxygen wasted with each combustion. On the other hand, combustion is complete with all fuels under the conditions existing in the combustion chamber, and consequently very reliable results may be obtained. In practice, however, it is much more important to know which of a given set of samples has the highest heating power, than to obtain very accurate figures; or, in other words, comparative values are of more importance than absolute values. Coal, in particular, varies in calorific value considerably according to the time and conditions under which it has been kept, and consequently a figure obtained for the calorific power applies only to a particular set of conditions, and can only be regarded as approximate for the varied circumstances under which the coal is used. Kroeker has also pointed out that all calorimeters of this type give higher results for a fuel containing hydrogen, than that which represents the actual heat developed under working conditions; as the water formed by the combustion in the calorimeter condenses, and gives out latent heat to the extent of 537 calories per gram, whereas no such condensation occurs in a furnace. If 1 gram of a fuel containing 5 per cent. of hydrogen were experimented with, the weight of water produced would be .45 gram, which, on condensing, would give out 242 calories. Kroeker's calorimeter enables the amount of water formed to be estimated, and the correction from this source is deducted from the result of the combustion. The chief value of the accurate results of a bomb calorimeter is that the figures serve as standards of comparison, and may be used to check the results obtained by simpler and more expeditious methods.

Darling's Calorimeter.—The principle adopted in this instrument is to burn the fuel in a stream of oxygen, and to allow the hot gases.

to bubble through the water surrounding the combustion chamber. In early forms of calorimeters of this type, the gases were allowed to escape through a few large holes into the water, in which case the total extraction of heat from the bubbles is doubtful. Wedmore introduced an improvement by causing the hot gases to escape through a series of fine perforations, which is the principle adopted in the calorimeter designed for fuels in general by the author. Fig. 2 shows the apparatus as fitted for gaseous fuels; Fig. 3 for solid fuels,

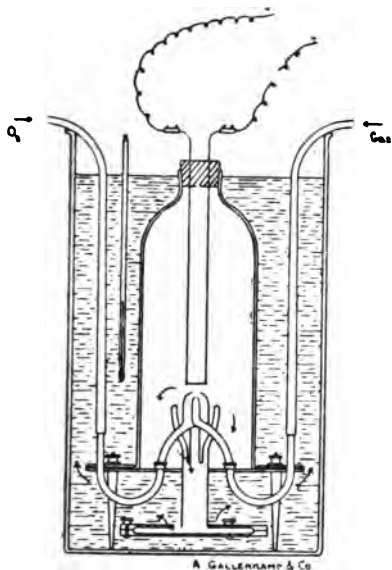


FIG. 2.—DARLING'S CALORIMETER,
FITTED FOR GASEOUS FUELS.

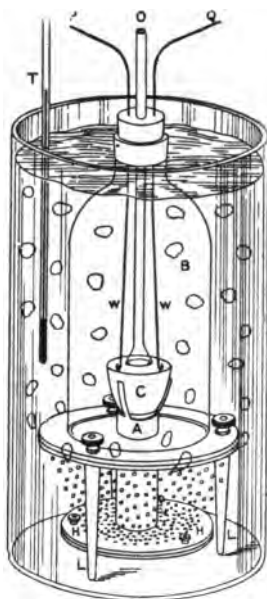


FIG. 3.—DARLING'S CALORI-
METER, AS USED FOR SOLID
FUELS (Gas fittings detached).

the fittings used for gases having been detached; and Fig. 4 shows the special arrangement adopted for liquid fuels. When used for solid fuels, 1 gram or thereabouts is carefully weighed into the crucible C (Fig. 3), which is held in position by three clips springing from the brass tube A. The author has found that nickel crucibles are quite as good as platinum for this purpose; and, in addition to being very durable, are extremely cheap. If porcelain crucibles be used, some of the fuel may escape ignition. The crucible is surrounded by a glass bell-jar, B, which has a flange on its lower rim

and is supported by a brass plate which rests on three legs, L. An air-tight joint is secured by allowing the flange of B to stand on a rubber ring, and clamping it down firmly by means of a brass covering ring and three nuts, which screw on to extensions of the legs L. The combustion is started by passing a current of electricity through a piece of platinum or iron wire embedded in the fuel, which is connected to thick copper wires passing through a rubber cork in the neck of the bell-jar to the leads P and Q. Oxygen is led into the combustion chamber from a cylinder or gas-holder by the tube O,

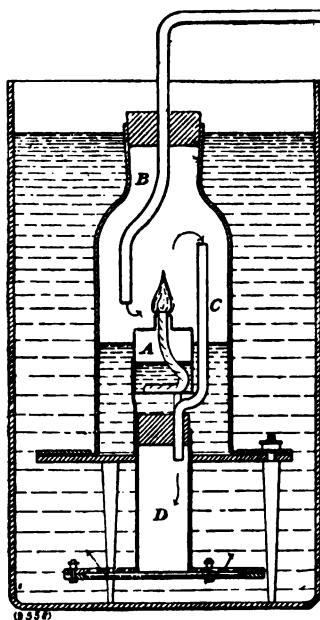


FIG. 4.—DARLING'S CALORIMETER AS USED FOR LIQUID FUELS.

which may be made of glass, and preferably furnished with a brass cone at the lower extremity. The hot products of combustion, mixed with excess of oxygen, pass through the tube A into a chamber made by fitting together two recessed brass plates, through the upper of which are drilled numerous fine holes, H, through which the gases escape. During the combustion the whole apparatus is immersed in water, to which the heat carried by the gases from the combustion chamber is imparted. The vessel containing the water may be made of glass or metal, and may be shielded from radiation by standing i

on cork or wooden supports in a larger vessel. The rise of temperature is observed by the thermometer T, which should be capable of reading to $\frac{1}{10}^{\circ}$ C., or $\frac{1}{10}^{\circ}$ F.

Instead of the device for electrical ignition, a small quantity of sulphur— $\frac{1}{10}$ of a gram is sufficient, or even less—may be used to start the ignition. In this case the sulphur is placed in a small heap on the top of the fuel, and touched with a hot rod, after which the cork is inserted in the bell-jar, a gentle stream of oxygen turned on, and the apparatus transferred rapidly to the vessel containing the water. This method of ignition is in many ways preferable to electrical ignition, and the heat produced by the sulphur may be deducted from the result. One gram of sulphur on burning in oxygen gives out 2200 calories; hence if $\frac{1}{10}$ of a gram has been used, 110 calories must be deducted from the result obtained.

The water equivalent of the apparatus is determined experimentally, and radiation readings may be taken if it be desired to apply a correction for this possible source of error. In practice, radiation errors may be largely eliminated by commencing with the water at a temperature as much below atmospheric temperature as the final reading is above the latter.

An example is given to illustrate the data required and method of calculation.

Sample taken : 1 gram of Welsh steam coal.

Initial temperature of water = 16.2° C.

Final " " = 21.3° C.

Weight of water taken = 1400 grams

Water equivalent of apparatus = 252 "

Ignited by $\frac{1}{10}$ of a gram of sulphur.

Calorific power

$$= \frac{(\text{weight of water} + \text{water equivalent}) \times \text{rise in temp.}}{\text{weight of fuel used}}$$

$$= \frac{(1400 + 252) \times 5.1}{1}$$

$$= 8425 \text{ calories per gram.}$$

Deducting 110 calories for sulphur used, the corrected value is 8315 calories per gram.

When liquid fuels are to be tested, the calorimeter is arranged as in Fig. 4. A quantity of the liquid is placed in a small brass lamp, A, furnished with an asbestos wick, and the lamp and its contents

weighed before placing in the clips used to hold the crucible when solid fuels are burnt. The brass tube from which the clips spring is closed by a rubber cork, through which passes a glass tube C, bent as shown, through which the hot products of combustion escape. This enables the lamp to be surrounded by water during the combustion, and so ensures tranquil burning. In the absence of such a cooling arrangement, the heat of combustion would boil the residual liquid in the lamp, and give rise to an explosion. The oxygen delivery-tube is bent, so that it may not come into contact with the flame of the burning fuel, and the direction of the escaping gases is as indicated by the arrows. Ignition may be commenced by lowering a lighted match into the combustion chamber, or by passing an electric spark across the wick. After burning has entirely ceased the lamp is removed, carefully dried, and re-weighed, the loss in weight representing the fuel burnt. The calculation is then made as for solid fuels. The most volatile liquid fuels may be safely tested in this way, it being necessary, however, to use a very narrow wick (about $\frac{1}{16}$ inch diameter) for light petrols, whilst for alcohol and ordinary petroleum the diameter may be $\frac{3}{16}$ inch.

When used for combustible gases, two brass tubes are passed through the plate on which the glass cover rests, and are connected by unions with an arrangement similar to a blowpipe (Fig. 2). The gas under test is burnt at a fine jet, oxygen being passed into the tube which surrounds the jet. Ignition is commenced by an electric spark, and the supply of gas is measured by mercury displacement or a suitable meter. The calculation is made as before, the calorific value being referred to 1 litre of the gas. The evaluation of a gaseous fuel by this calorimeter requires considerable experimental skill; the apparatus being better adapted for solid and liquid fuels than for gaseous.

In this calorimeter the combustion is visible and under the control of the operator, and no special skill is requisite to conduct an experiment. Results may be obtained which do not differ from those of a bomb calorimeter by more than 1 or 2 per cent.; which falls well within the possible alterations of a solid fuel on keeping. It is customary to perform the routine tests with one of these calorimeters, reserving cases where special accuracy is required for a bomb calorimeter.

Junker's Calorimeter for Gaseous Fuels.—In this instrument the gas to be tested is burnt in a Bunsen or Argand burner, the heated products of combustion passing over a series of metal pipes through which water is flowing, and which serve to absorb the heat generated

by the flame. In working the instrument, the burner is first ignited, and a steady stream of water passed through the pipes, until stationary temperatures are registered on two thermometers, one of which is placed in the water at the point of entrance, and the other at the exit. The reading of a gas-meter attached to the supply pipe is now taken, and a 2000 c.c. measure placed so as to collect the escaping water. When the measure is filled to the mark, the gas-meter is again read, and the volume of gas burnt is thus obtained. The calculation is illustrated by the following example:—

In testing a sample of coal gas the entering water was at 16°C. , and the escaping water at 21°C. During the collection of 2000 c.c. of water, .058 cubic foot of gas was burnt. Hence $2000 \times (21-16) = 10,000$ calories were produced by the combustion of .058 cub. ft. of the gas, or 17,240 calories per cubic foot. Dividing calories by 252 to convert into B.Th.U., the result obtained is 684 B.Th.U. per cubic foot.

The Junker gas calorimeter, which has been modified by Simmance-Abady and Boys, is now the recognised apparatus for the commercial evaluation of gaseous fuels. In testing producer gas a difficulty sometimes arises owing to the choking of the meter by tarry matter carried by the gas. This trouble is best overcome by passing electric sparks continuously through the gas in front of the entrance to the meter, which effect the deposition of the particles of tarry liquid. The rate of flow of the water should be such that about 5 minutes are occupied in the collection of 2 litres.

Calorimeters in which the Fuel is mixed with a Solid Oxygen Provider.—In calorimeters of this type the fuel is mixed with a solid or solids which furnish oxygen, the mixture forming a kind of fireworks, which is caused to ignite in a diving-bell under water. A well-known instrument is that of Lewis Thompson, illustrated in Fig. 5. Two grams of finely-divided fuel are mixed with 26 grams of "combustion mixture" (potassium chlorate, 3 parts; potassium nitrate, 1 part). The mixture is introduced into a copper cylinder, C, which is then fixed into position on the base of B. A fuse, made of wick, soaked in a solution of saltpetre, and dried, is placed with its lower end embedded in the mixture. The upper end of the fuse is ignited, and the cover, D (which, when the tap is closed, forms a diving-bell), is rapidly placed over the combustion cylinder, where it is held in position by flexible tongues of metal placed on the base B. The whole arrangement is now rapidly transferred to the vessel V, which contains a known quantity of water at a known temperature. When the fuse burns down to the contents of the copper cylinder, vigorous

combustion takes place, the gases produced passing through the holes at the lower part of D, and rising to the surface of the water. In rising, the bubbles are deprived of the excess temperature they possess by the water, and should fall to the temperature of the latter before escaping into the air. When no more bubbles escape, the tap is opened, allowing the water to rise in D and submerge the combustion cylinder. The water is then mixed and the temperature taken. The calorific power is found, as in the previous cases, from the expression

$$\frac{(\text{weight of water} + \text{water equivalent}) \times \text{rise of temp.}}{\text{weight of fuel burnt}} \cdot$$

The drawbacks of this instrument are (1) complete combustion is seldom secured, particularly in the case of anthracite, coke, and

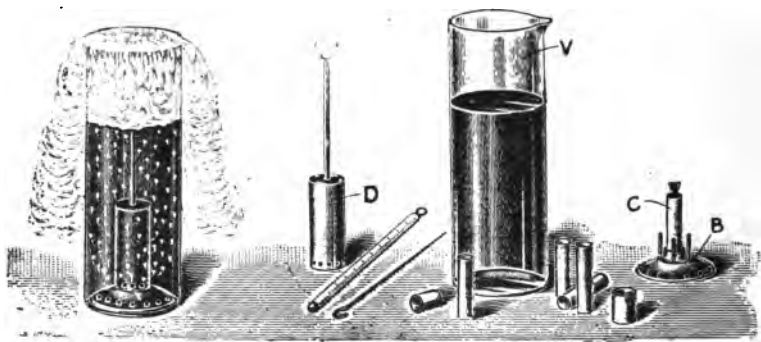


FIG. 5.—LEWIS THOMPSON'S CALORIMETER.

fuels containing a high percentage of fixed carbon ; (2) a certain amount of chemical heat is disengaged by the breaking-up of the potassium chlorate, which is an endothermic substance ; (3) the fuse sometimes fails to act, or ignites the mixture before the apparatus has been immersed in the water ; and (4) the bubbles of gas are large and escape rapidly, leaving the water before being entirely deprived of the surplus heat they possess. Consequently, the results obtained are in general lower than the figures furnished by other types of calorimeter.

Parr's calorimeter differs from Lewis Thompson's in several details. The fuel is mixed with barium peroxide or sodium peroxide, and placed in a cartridge sealed by a valve, through which a piece of hot copper wire is dropped to commence the ignition. The

carbon dioxide and water produced are absorbed by the peroxide; no gases therefore escape. The heat produced is due partly to the combustion of the fuel, and partly to the chemical union of the products with the sodium or barium compound. In the case of an average coal, 73 per cent. of the total heat is found to be due to the combustion proper, and consequently 73 per cent. of the total heat units evolved by 1 gram of coal, when burnt in the calorimeter, is taken as the calorific power. During the experiment the combustion chamber, which is furnished with projecting arms, is caused to rotate by means of a small motor, thus acting as a stirrer to the water.

Commercial Uses.—Calorimeters of the Lewis Thompson and Parr type are useful in places where a supply of oxygen gas cannot readily be obtained. The results are not so reliable as those obtained by direct combustion in oxygen, nor are these calorimeters so expeditious as those employing free oxygen, owing to the time taken in mixing the fuel with the chemical ingredients, and the subsequent cleaning of the cartridge or combustion chamber.

Methods of Expressing Results.—The figure obtained for the calorific value of a fuel by any of the foregoing methods expresses the number of calories evolved on burning 1 gram of the fuel. The conversion into units involving the *pound* or degree Fahrenheit may be readily made. Thus, if

1 gram of fuel evolves 8000 calories,

then x grams „ evolve $(8000 \times x)$ calories,

or x grams „ will raise $(8000 \times x)$ grams of water 1°C .

If $x = 453.6$ (number of grams in 1 lb.), it follows that 1 lb. of fuel will raise 8000 lb. of water 1°C . That is, the figure expressing calories per gram also expresses lb.- $^\circ \text{C}$. units per lb.

To convert into B.Th.U., the figure must be multiplied by $\frac{9}{5}$ or 1.8, as an interval of temperature of 1°C . = 1.8°F .

8000 calories per gram therefore equal 8000 lb.- $^\circ \text{C}$. units per lb. = $8000 \times 1.8 = 14,400$ B.Th.U. per lb.

It is customary also to express the results in terms of *evaporative power*, that is, the number of grams (or lb.) of water at 100°C ., which would be converted into steam at 100°C . by the heat furnished by 1 gram (or lb.) of fuel. This figure is obtained by dividing the calorific power by the number expressing the latent heat of steam at 100°C ., which in Centigrade units is 537 calories per gram, or 537 lb.- $^\circ \text{C}$. units per lb.; or 967 B.Th.U. per lb. Hence

the evaporative power of a fuel of calorific value 8000 calories per gram will be

$$\frac{8000}{537}, \text{ or } \frac{14,400}{967} = 14.9.$$

This is only the theoretical figure, as in any practical boiler a considerable portion of the heat escapes with the hot gases up the flue, besides losses by radiation, etc.

Interpretation of Results.—The values obtained with samples of coal vary considerably, according to the composition. A good Welsh steam coal will be found to possess a calorific power exceeding 8000 calories per gram; specimens from other localities falling between 7000 and 8000. A result less than 7000 calories per gram = 12,600 B.Th.U. per lb., indicates an inferior specimen. Average samples of coke should yield about 6000 calories per gram = 10,800 B.Th.U. per lb. Calorific power alone, however, is not sufficient to determine the choice of a fuel. Other considerations, such as the rate of burning; the tendency to produce smoke and thus burn wastefully; the amount of ash present, which forms clinkers and thus tends to choke the firebars; and the amount of sulphur, which causes corrosion of the furnace, must also be taken into account. The cost is also of great importance, and it is generally necessary to resort to practical trials before the most suitable fuel for a given purpose can be discovered.

Liquid fuels, in the form of petroleum or petroleum extracts, should possess a calorific value approximating to 11,000 calories per gram, or 19,800 B.Th.U. per lb. The volatile portions are specially suitable for the internal combustion engines now so common in motor vehicles, whilst heavy varieties or residues may be used for steam raising or small furnaces.

The calorific value of gaseous fuels varies widely, according to the nature of the gas. This is indicated by the figures appended for four varieties:—

Name	Calorific Power	
	Lb.-°C. units per cubic foot	B.Th.U. per cubic foot
Pittsburg natural gas . .	495	891
Producer gas (Siemens) . .	111	200
Coal gas (average) . .	378	680
Water gas (best) . . .	193	347

The difference in the values is due to difference in composition.

British Coals: Varieties, Properties and Uses.—The composition, and consequently the properties, of coal differ considerably, and a classification of the chief varieties may be made accordingly, as shown in the following table:—

Name of Coal	Percentage of			
	Carbon	Hydrogen	Oxygen	Ash, Sulphur, etc.
Anthracite	91·5	3·5	2·6	2·4
Dry bituminous . .	87	5	4	4
Caking	85	5	6	4
Cannel	84	6	8	2
Dry long flaming . .	77	5	15	3
Lignite	70	5	20	5

The first two varieties occur largely in South Wales, and possess a higher calorific power than the remainder. The amount of gaseous constituents is lowest in anthracite, which for this reason is more difficult to burn than other classes of coal. Coal rich in gaseous ingredients generally burns easily and rapidly, giving a considerable amount of flame, but is usually inferior in calorific value to a coal rich in carbon, which does not produce much flame. Gaseous coals also tend to produce smoke, which is due to the imperfect combustion of gaseous hydrocarbons which distil from the coal. Anthracite and dry bituminous coal, on the other hand, are practically smokeless. The coalfields of Britain, other than South Wales, yield coal of a gaseous character.

The table on next page, compiled from the figures obtained in the Admiralty Coal Investigation, shows the differences between the coal derived from different localities.

It will be seen from the table that the Welsh samples are superior in respect to evaporative power, and in addition occupy less space, weight for weight, than the remainder. The slow burning of Welsh coal is also indicated in the table, as the number of pounds of water evaporated per hour is practically the same as that of the Lancashire coal, which is much inferior in evaporative power, but burns more rapidly, entailing more frequent stoking. The general superiority of Welsh coal, whenever sufficient draught is available, has been well

Locality	Practical Evaporative Power (in boiler furnace)	No of lbs. Evaporated per hour	Percentage of Ash	Specific Gravity	Space Occupied by 1 ton in cubic feet
Average of :—					
37 samples from Wales .	9.05	448.2	4.91	1.315	42.71
17 „ „ Newcastle .	8.37	411.1	3.77	1.256	45.30
28 „ „ Lancashire .	7.94	447.6	4.88	1.273	45.15
8 „ „ Scotland .	7.70	431.4	4.03	1.259	49.99
8 „ „ Derbyshire .	7.58	432.7	2.65	1.292	47.45

established by repeated trials. Amongst the many varieties of Welsh coal the best known are Nixon's Navigation, Powell Duffryn, Hill's Plymouth, and Wayne's Merthyr. In a good form of boiler any of these kinds show a practical evaporative power of about 10, and differ from each other very slightly. Welsh steam coals in general are in great demand for steam-raising purposes, particularly on steamships. The comparatively high cost is balanced by the steady burning, high evaporative power, comparatively small amount of ash, and the absence of smoke.

Coal from other localities, being in general easier of combustion than Welsh coal, is adapted for uses in which a strong draught is not available, as in the case of domestic fires, locomotives, and small stationary boilers. The highly gaseous varieties are used for the manufacture of gas; the residue, or coke, being employed in metallurgical and other operations. Gaseous coals are also used in obtaining the high temperatures requisite in various furnaces used in the treatment of metals. Owing to the cost of transit, ordinary coal is frequently used in cases where Welsh coal would be more suitable, but less economical.

Amount of Air required to burn Coal.—The oxygen present in the air only constitutes $\frac{1}{5}$ of the total volume, the remaining $\frac{4}{5}$ not taking part in the combustion of fuel. When the composition of a fuel is known, the amount of air requisite for combustion may be calculated from chemical data. One gram of carbon requires 1.86 litre of oxygen (measured at 0°C. and 760 mm. pressure) for complete combustion; and 1 gram of hydrogen combines with 5.58 litres of oxygen. Hence if the proportion of carbon and hydrogen in a fuel be known, the volume of oxygen required for combustion may be calculated. The result, multiplied by 5, will give the requisite volume of air necessary exactly to burn the fuel. In practice, however, a

greater quantity must be admitted to a furnace, as the air is not in contact with the fuel for a sufficient time to enable all the oxygen to be consumed. An excess of $\frac{1}{3}$, or 33 per cent. above the theoretical quantity, is found most economical in practice, and the spacing of firebars and draught of the chimney should be such as to admit this quantity to the fuel. A larger excess is wasteful, as it merely serves to carry heat away into the flue. An average coal requires, theoretically, about 12 lb. of air (which at 60° F. occupies a volume of 157 cubic feet) to burn 1 lb. completely. Adding $\frac{1}{3}$, the volume of air admitted to a furnace to ensure good combustion should be 210 cubic feet for every pound of coal burnt.

Smoke Prevention.—The smoke produced on burning fuels rich in volatile matter is due to the distillation of heavy hydrocarbons from the fuel, which are decomposed by the heat yielding free carbon. If the hydrocarbons escape suddenly, the soot produced is carried by the draught into the flue before the particles have attained the temperature of ignition, thereby giving rise to smoke. Many appliances have been devised with a view to preventing smoke, but none have proved completely successful. The aim in smoke-prevention apparatus is either to admit an additional quantity of air to the furnace, so as to consume the carbon or soot; or to stoke the furnace gradually from the forward end, so that no large generation of soot takes place suddenly. The extra quantity of air is brought into the furnace either by an induced draught created by a fan placed in the flue, or by aspirating air through or over the fuel by the aid of steam-jets. Gradual stoking is accomplished by mechanisms which feed the fuel forward at any desired rate; many mechanical stokers having been devised for this purpose. Smoke prevention arrangements can only be applied to comparatively large plant, and no practicable scheme has yet been devised to prevent the smoke arising from domestic fires, locomotives, and small stationary plant. Liquid fuels are liable to give rise to smoke, unless care is taken in the control of the furnace; and the experience of many years' trial of various smoke-prevention apparatus points to the conclusion that careful stoking, combined with a judicious selection of fuel, is the best means of reducing smoke to a minimum. The introduction of cheap gaseous fuel, such as Mond's gas, is very desirable from the standpoint of smoke abatement.

Liquid Fuels.—The use of liquid fuels has greatly extended in recent years, not only for internal combustion engines, but also for steam raising and small furnaces. The various petroleum distillates and residues represent the chief source of liquid fuel; alcohol being

used to a small extent only. The lighter petroleum extracts, known as petrol, etc., are suited to high speed internal combustion engines, such as are used to propel motor vehicles. The heavier portions and residues have been successfully employed in producing heat for various purposes.

The petroleum obtained from various sources (Russia, America, etc.) possesses approximately the same calorific power, which averages 11,000 calories per gram or 19,800 B.Th.U. per lb. The specific gravity of crude petroleum ranges from 0.938 to 0.884; the lighter distillates having a specific gravity of 0.7 and upwards. Weight for weight, the heating power of petroleum is about $\frac{1}{3}$ greater than that of good coal. In oil engines the vapour of the oil is exploded with air in the cylinder, the heat generated by the action furnishing the motive power. When used for producing heat, the petroleum is injected into the furnace in the form of a spray, sufficient air being also admitted to secure proper combustion. The chief advantages of liquid fuels are: (1) Greater calorific power than coal, resulting in a reduction in weight of fuel of over 30 per cent. for a given heating effect; (2) Occupies less space than solid fuel; (3) More convenient to store and load; (4) Greater speed in getting up steam; (5) Complete control over the combustion, which may be stopped instantaneously, or reduced as required. The chief drawbacks are: (1) Danger of explosion of the stored oil; (2) Loss by evaporation; (3) Cost, which is largely a question of locality.

Experiments conducted on the South-Eastern Railway of Russia showed that in that locality, under the prices prevailing for coal and petroleum, a saving of 70 per cent. was effected by using petroleum instead of coal for the locomotives. On many steamships, and also on the locomotives of the Great Eastern Railway of England, petroleum has been used to feed coal fires, with economical results. Mr. Holden, of the Great Eastern Railway, employed petroleum residue, known as "astatki," with a resultant saving of 2.14 per cent. on the cost of coal, but has recently abandoned the use of liquid fuel for other reasons. The use of petroleum fuel, either alone or as an auxiliary to coal, is extending in many directions, notably to steamships and small furnace operations. The time and labour saved in coaling is an important factor in the case of steamships; and in small furnaces the extra cleanliness and easy control are considerations which frequently outweigh the extra cost of the petroleum.

Gaseous Fuels.—Many important metallurgical processes are conducted with the aid of gaseous fuel, notably the Siemens-Martin steel process, which has now largely supplanted other methods.

Re-heating and other furnaces also employ gaseous fuel ; and, in addition, gas is extensively used as a prime motor in the various types of gas engine. In the United States of America, Russia, China, and other places, large stores of combustible gases are obtained from the earth, and are known as "natural" gas. Manufactured gas is obtained by one of three chief processes, viz. : (1) By the distillation of coal in closed resorts, producing *coal gas* ; (2) By burning fuel in a limited supply of air, to which steam is added, forming *producer gas* ; (3) By passing steam over red-hot coke or anthracite, giving *water gas*. Coal gas is used for illuminating purposes and gas engines ; producer gas is chiefly used for the production of heat in furnaces. The gases escaping from blast furnaces are used for heating purposes, and have been shown by Bryan Donkin to be sufficiently combustible for use in gas engines of special construction, and a number of installations are already in use in which the motive power is furnished by these gases.

The combustible constituents of gaseous fuels are chiefly hydrogen, marsh gas (CH_4), carbon monoxide (CO), and small quantities of other hydrocarbons. The proportions of the constituents vary with the origin of the gas, and a quantity of non-combustible gases are also present. The calorific value is highest in the case of gases rich in marsh gas and other hydrocarbons. A table is appended, showing the composition and calorific value of gases from different sources.

Name	Percentage of						Calorific Value in B.Th.U. per cubic foot
	Carbon Mon-oxide	Carbon Dioxide	Hydro-gen	Marsh Gas	Nitro-gen	Other Gases, chiefly Hydro-carbons	
Pittsburg natural gas	1·0	0·8	22·02	72·18	nil	6·0	891
Siemens' producer gas (best quality)	22·23	6·1	28·7	1·0	41·9	nil	200
Coal gas (average)	6·64	3·67	45·58	34·90	2·46	6·75	680
Water gas (best)	35·88	2·05	52·76	4·11	4·43	0·77	347
Mond's producer gas	13·2	12·9	24·8	2·3	46·8	nil	155

Mond's gas is an extremely cheap form of producer gas, made from a cheap bituminous coal slack. Arrangements exist in the

process for the recovery of ammonia, which in other producers is wasted. The value of the recovered ammonia is equal to the cost of the fuel used, the only charges being labour and upkeep of the plant. The gas may be used for metallurgical processes and gas engines, and its cheapness renders it an economic source of heat and power. The distribution of the gas for manufacturing purposes from a large central station is being tried in Staffordshire, and should the result prove economical and successful the use of Mond's gas will extend largely. One beneficial result of such an extension would be the mitigation of the smoke nuisance.

During the last few years, gas generators working on the "suction" system have been introduced for the direct working of gas engines. The charge of gas is drawn into the engine directly from the producer, in which a mixture of air and steam is drawn over red-hot anthracite by the action of the engine. After discharging the exhaust gases, the cylinder is in direct communication with the producer, and the back stroke of the piston causes a fresh quantity of air and steam to pass over the anthracite. A cheap form of gaseous fuel is thus generated as required, the result being to furnish an extremely cheap source of power, as well as a self-contained plant. The use of suction plant is in consequence extending rapidly.

The low heating power of producer gas is due to the large amount of nitrogen present, derived from the air used in the manufacture. A considerable quantity of carbon dioxide, also an inert constituent, is also present. The calorific values of the three chief combustible constituents, expressed in B.Th.U. per cubic foot, are as follows: marsh gas, 1050; hydrogen, 344; carbon monoxide, 342.

Methods of producing High Temperatures; Electric Furnaces.—In using fuel for steam boilers an extremely high temperature is not desirable, and, if obtained, would result in the loss of a considerable quantity of heat owing to the high temperature of the waste gases. In metallurgical operations, however, a very high temperature is frequently requisite for the success of the process. Where coal or coke is employed, the required temperature is obtained by the use of a blast or forced draught of air, which renders the combustion more rapid than if burnt under normal conditions. The rapid combustion gives rise to a high temperature, which in the case of coal or coke may be made to approximate 1800° C., or 3240° F., a temperature which will melt all ordinary metals.

When gas is used as a fuel for furnaces in which a very high temperature is desired, the method in general use is known as the "regenerative" system, and is due to Sir W. Siemens. In this

system, which is now almost universal in steel-making processes, the products of combustion are caused to pass through a network of firebricks, which are heated thereby. Two pairs of firebrick chambers are provided, and by an arrangement of valves the air and gas may be admitted through either pair to the bed of the furnace, where they mix and burn. At the commencement air and gas are admitted through one pair of chambers, the products passing through the other pair. On reversing the valves the air and gas are each heated by passing over the hot firebricks, and enter the furnace at a comparatively high temperature, which augments the temperature produced by burning the gases under ordinary conditions. Thus, if 1000°C . were obtained by burning the gas and air when used at atmospheric temperature, and if in the process the gas and air were heated to 200°C . before entering the furnace, the temperature produced would be nearly 1200°C . In consequence of the increased temperature, the firebricks through which the products escape will be hotter than before, and may attain, say, 400°C . On again reversing, the temperature in the furnace would be nearly 1400°C .; and consequently, any desired high temperature may be obtained by reversing periodically. The practical limit is the melting point of the furnace lining, and the theoretical limit is the temperature at which the chemical actions giving rise to the heat cease to be realised, or are so weak as to be practically inoperative.

The advances made in the cheap production of electricity on the large scale have led to the introduction of the electric furnace, which is capable of yielding a temperature higher than that obtainable by any other known method. Electric furnaces are being largely used in smelting operations, particularly in places where water power is available for generating current. The heating effect is obtained by the current passing through a resistance, and the temperature obtainable is at least 3700°C ., or 6660°F . In some electric furnaces the material to be operated on is fed through an electric arc; in other cases the material is placed on a carbon grid, which is heated to the desired temperature by regulating the current. In another form a refractory chamber is heated externally by surrounding it with powdered carbon, or a mixture of graphite and fireclay, through which the current is passed. In certain small operations graphite tubes are heated by the current, the material being placed in a carbon vessel inside the tube. Fresh forms of electric furnaces are continuously being devised, and will doubtless play an important part commercially in the future. The cost of producing a given quantity of heat by electricity is much greater than in the case of fuel; but in many

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processes other advantages more than compensate this item. Further, owing to the extremely high temperature attainable, an entirely new field has been opened for the production of materials which cannot be otherwise obtained. An example is calcium carbide, which when acted on with water yields acetylene, and is now of much commercial importance.

A method of producing high temperatures has recently been introduced by Goldschmidt, who employs a mixture of powdered aluminium and oxide of iron, the mixture being known as "thermit." When this mixture is ignited by a special fuse, an exceedingly high temperature, approximating to that of the electric arc, is obtained. The action results in the production of oxide of aluminium and metallic iron. The process has been applied to welding pipes, rails, etc.; the operation consisting in igniting "thermit" placed round the junction of the separate pieces, when the heat produced melts the metals at the junction and causes complete fusion.

On the small scale high temperatures, exceeding $2000^{\circ}\text{C}.$, may be obtained by burning hydrogen, or better still, acetylene in a blowpipe fed with oxygen. The oxy-acetylene flame is now used to a considerable extent for small welding operations, the temperature produced being sufficient to melt iron readily, and to cause it to flow freely.

CHAPTER III.

SPECIFIC HEAT.

Thermal Capacity.—The addition of equal amounts of heat energy to equal weights of different substances does not cause the same rise in temperature. Thus 1 calorie, if imparted to 1 gram of water, causes a rise of $1^{\circ}\text{C}.$; but if imparted to 1 gram of mercury the temperature rises by about $33^{\circ}\text{C}.$ For 1 gram of iron the rise in temperature would be $9^{\circ}\text{C}.$; for 1 gram of aluminium $5^{\circ}\text{C}.$, and so on. If deprived of 1 calorie, a fall in temperature, equal to the rise on adding 1 calorie would be observed in each case. It is evident, therefore, that temperature alone does not indicate the *amount* of heat energy possessed by a substance, which must depend upon its capacity for storing heat, or *thermal capacity*.

Water possesses a greater thermal capacity than any other ordinary substance, being only exceeded in this respect by hydrogen, liquid ammonia, and certain mixtures of alcohol and water. From the above figures it will be seen that, compared weight for weight, the thermal capacity of water is 33 times as great as that of mercury, and 9 and 5 times as great as that of iron and aluminium respectively. For this reason water is a suitable substance with which to form a standard of thermal capacity, to which all other bodies are referred. Water possesses other advantages, however, which add to its suitability for this purpose, viz. the comparative equality of its thermal capacity at temperatures between $0^{\circ}\text{C}.$ and $100^{\circ}\text{C}.$; the fact that it is always available for experimental purposes; its use involves no cost; it is not a corrosive liquid to any great extent, and does not evaporate readily at ordinary temperatures. For these reasons the thermal capacities of all substances are expressed in terms of that of water, which is taken as unity.

Specific Heat.—The ratio of the thermal capacity of a substance to that of water is termed its "specific heat," which may be defined as the ratio of the amount of heat required to raise a given weight of the substance through a given temperature, to that required to raise an equal weight of water through the same temperature. By taking

1 gram as unit weight, and 1°C. as the rise of temperature, the definition becomes :—

$$\frac{\text{Heat units required to raise 1 gram of substance } 1^{\circ}\text{C.}}{\text{Heat units required to raise 1 gram of water } 1^{\circ}\text{C.}}$$

Taking the calorie as heat unit in each case, the denominator becomes equal to unity, as 1 calorie will raise 1 gram of water 1°C. by definition. Hence the specific heat of a substance is equal to the number of calories required to raise the temperature of 1 gram 1°C. It should be observed that the same figure is given by the number of lb.- $^{\circ}\text{C.}$ units required to raise 1 lb. of the substance 1°C. ; or by the number of B.Th.U.'s required to raise 1 lb. of the substance 1°F. The specific heat of water is unity.

Example 1.—A substance of specific heat $\cdot 11$ would require $\cdot 11$ calorie to cause a rise of temperature of 1°C. for each gram of substance.

Hence

453.6 grams (= 1 lb.) require $453.6 \times \cdot 11$ calories per $^{\circ}\text{C.}$

But 453.6 calories = 1 lb.- $^{\circ}\text{C.}$ unit.

Therefore

1 lb. requires $\cdot 11$ lb.- $^{\circ}\text{C.}$ units for 1°C. rise of temp.

Similarly

1 lb. would require $453.6 \times \cdot 11 \times \frac{5}{9}$ calories per $^{\circ}\text{F.}$,
as a rise of 1°F. only represents $\frac{5}{9}^{\circ}\text{C.}$

But $453.6 \times \frac{5}{9} = 252$ calories = 1 B.Th.U.

Hence

1 lb. raised 1°F. requires $\cdot 11$ B.Th.U.

Example 2.—Twenty grams of a substance of specific heat $\cdot 21$, when cooled from 60°C. to 40°C. , would give out $20 \times \cdot 21 \times (60-40)$ calories = 84 calories.

Experimental determination of Specific Heats.—Four chief methods exist for determining the specific heat of a substance, and are known as

1. The method of mixtures
2. Method of fusion.
3. Condensation method.
4. Cooling method.

Each of these will now be described.

Method of Mixtures.—This method was employed by Regnault in his experiments on specific heats, and is a simple and accurate means of obtaining the value in the case of solids and liquids, and also for gases at constant pressure. When the specific heat of a solid is to be found, it is heated to nearly 100°C . in a vessel surrounded by steam, and then allowed to fall into a known quantity of cold water. After permitting the solid and water to attain the same temperature, the rise in degrees is noted, and the specific heat calculated from the data obtained. Fig. 6 shows the apparatus, which consists of the double vessel A, in the inner of which the solid is placed. Steam from a boiler circulates in the space between the vessels, and after a few minutes the solid will have attained a steady temperature (never quite equal to that of the steam), which is recorded on the thermometer placed in contact with the solid. The water is weighed out in a vessel or calorimeter, B, made of thin copper or silver, and suspended in a larger vessel or shield, which is intended to protect the inner vessel from loss or gain of heat due to the surroundings. The temperature of the cold water is taken with a delicate thermometer, and the hot solid rapidly dropped in. The water is then stirred until a steady temperature is obtained, and the result calculated as under :—

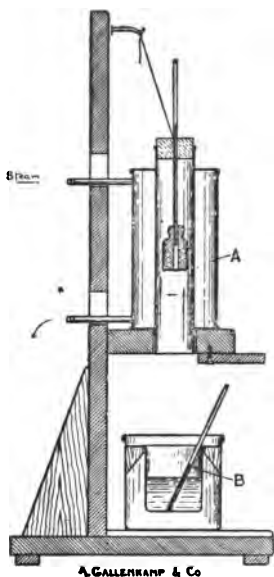


FIG. 6.—APPARATUS FOR SPECIFIC HEATS BY METHOD OF MIXTURES.

	Heat units lost by solid	= Heat units gained by water and calorimeter.
but	Heat units lost by solid	= Weight \times specific heat \times fall in temp.
and	Heat units gained by water	= Weight \times rise in temp.
also	Heat units gained by calorimeter	= Weight \times specific heat of material \times rise in temp.

The equation therefore becomes—

$$\begin{aligned}
 & (\text{Weight of solid} \times \text{specific heat} \times \text{fall in temp.}) \\
 & = (\text{Weight of water} \times \text{rise in temp.}) + (\text{weight of calorimeter} \\
 & \quad \times \text{specific heat of its material} \times \text{rise in temp.})
 \end{aligned}$$

It is presumed that the specific heat of the material of which the calorimeter is made is known, and consequently in the above equation the only unknown quantity is the specific heat of the solid, which is calculated from the data furnished by the experiment.

Example.—250 grams of copper are immersed in 150 grams of water at 20° C., contained in a calorimeter weighing 100 grams, made of material of specific heat .1. The temperature of the mixture is 30.3° C. Find the specific heat of the copper.

Inserting values in the equation given above—

$$250 \times \text{specific heat} \times (100 - 30.3) = (150 \times 10.3) + (100 \times .1 \times 10.3)$$

From which the value of the specific heat is .0946.

It is evident that the product “(weight of calorimeter \times specific heat of its material)” has a constant value, and is equal to the weight of water which would take up an equal amount of heat. Thus if the calorimeter weigh 50 grams, and the material have a specific heat of .1, then a rise of 1° C. would require $(50 \times .1) = 5$ calories. The weight of water which would be raised 1° C. by 5 calories = 5 grams; or, in general, x calories will raise x grams of water 1° C. Hence the product “wt. of calorimeter \times sp. heat of material” gives a figure which represents the number of grams of water equal in thermal capacity to the calorimeter. Hence this product represents the “*water equivalent*,” which may be added to the actual water taken in order to simplify the calculation, which then becomes.—

$$(\text{wt. of solid} \times \text{sp. ht.} \times \text{fall in temp.}) = (\text{wt. of water} + \text{water equiv.}) \times \text{rise in temp.}$$

Calorimeters for determinations of this kind are made of copper or silver, both of which are good conductors of heat; and consequently the portions of the vessel above the water will nearly attain the temperature of the parts in contact with the water. This would not be the case if glass, or other bad conductor, were used; and the quantity of heat absorbed by the calorimeter would then be uncertain, and would require a special experiment to determine. It should be noted that the outer vessel, or shield, does not participate in the gain of heat due to the hot solid, and therefore does not enter into the calculation. It will avoid confusion if it be remembered that the term “calorimeter” applies only to the parts which are

affected by the rise in temperature. Expressed in symbols, the equation giving the specific heat is

$$S = \frac{(W_1 + w) \times (t_2 - t_1)}{W \times (t - t_2)}$$

where S = specific heat of solid.

W = weight of solid.

t = temperature of solid before immersion.

W_1 = weight of water.

w = water equivalent of calorimeter.

t_1 = initial temperature of water and calorimeter.

t_2 = final " " " "

In refined experiments the water equivalent of the thermometer should be added to w , but is usually a small quantity, falling within the limits of other experimental errors.

The method of mixtures may be applied to liquids also, by employing a solid of known specific heat, which is dropped into a calorimeter containing the liquid under experiment. The procedure is the same as for solids, but the calculation differs slightly as shown.

Heat given out by solid = heat taken up by liquid.

$$\begin{aligned} \therefore & \quad (\text{wt. of solid} \times \text{sp. ht.} \times \text{fall in temp.}) \\ & = (\text{wt. of liquid} \times \text{sp. ht.} \times \text{rise in temp.}) \\ & \quad + (\text{water equiv.} \times \text{rise in temp.}) \end{aligned}$$

Or, in symbols,

$$S = \frac{\{(W \times x) \times (t - t_2)\} - \{w \times (t_2 - t_1)\}}{W_1 \times (t_2 - t_1)}$$

where

S is the specific heat of the liquid

x " known heat of the solid

W_1 " weight of liquid taken

the remaining symbols having the same significance as before.

Example.—To determine the specific heat of turpentine a piece of copper (specific heat = .093), weighing 100 grams, was heated to 98.2°C . and dropped into 125 grams of the turpentine, initially at 18.7°C . The temperature after mixing was 28.2°C ., and the water equivalent of the vessel 12 grams. This gives the specific heat of turpentine as .452.

When a solid is soluble in water, the specific heat may be obtained by allowing it to fall into a liquid of known specific heat, in

which the solid is insoluble. The calculation is made, as usual, by balancing the loss of heat to the gain. It should be observed that when a liquid other than water is used in the calorimeter, the water equivalent must not be added to the weight of the liquid, but the calculation performed in detail.

The values obtained by the method of mixtures represent only the *mean* or *average* specific heat of the substance between the temperatures employed, as the calculation presumes that an equal amount of heat is given out for each degree during the fall in temperature. This is seldom the case, as at higher temperatures most substances give out a greater amount of heat on falling through 1° than at lower temperatures. Or, in general, the specific heat increases with the temperature, which it is therefore necessary to specify in connection with any given value.

The specific heat of gases will be reserved for special consideration.

Method of Fusion.—This method is based on the principle that a fixed number of heat units are required to melt 1 gram of ice at 0° C., producing water at 0° C. The heat is expended in producing the physical change, and is spoken of as “latent” heat. The latent heat of fusion of 1 gram of ice is 80 calories.

Black, who first used this method, used a block of ice in which a cavity had been made, which could be covered by another slab of ice. After carefully drying out the cavity with blotting paper, the weighed substance, at a known temperature, was dropped in, and covered over by the slab of ice. After remaining in the cavity until it had fallen to the temperature of the ice, the body was removed, and the amount of water collected in the cavity found by absorbing it in dry blotting paper (previously weighed) and weighing. The increase represented the weight of ice melted, and the specific heat was calculated from the equation—

Heat units lost by substance = Heat units gained by ice,
that is,

Wt. of substance \times S \times fall in temp. = Wt. of ice melted \times L,
where S = specific heat,
L = latent heat of fusion of ice.

Example.—On placing 150 grams of iron at 25° C. into a cavity in a block of ice, it was found that 5.1 grams of ice were melted. The specific heat of iron is therefore,

$$S = \frac{5.1 \times 80}{150 \times (25-0)} = .109 \text{ nearly.}$$

Lavoisier and Laplace improved the method, using a vessel containing broken ice, and furnished with a tap from which the water resulting from the fusion could be collected. This vessel was surrounded by a larger protecting vessel, also containing ice, which served to shield the inner one from external heat influences. In using the apparatus, the tap of the inner vessel was opened, and any water present allowed to drain out. The tap was then closed, and the substance inserted, the whole arrangement being covered by a lid. The water resulting from the melting ice was then run out at

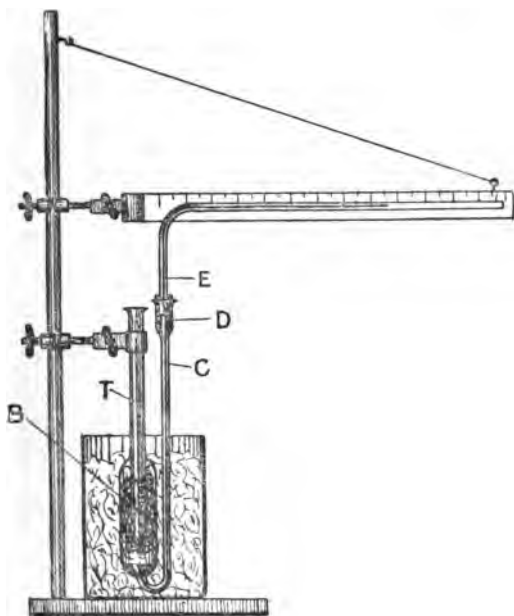


FIG. 7.—BUNSEN'S ICE CALORIMETER.

the tap and weighed, the result being calculated as in Black's experiment. The results were liable to error owing to the difficulty of preventing the water formed from clinging to the ice.

Bunsen's calorimeter is an arrangement in which the contraction produced by ice on melting is measured, the specific heat of the substance being deduced from the contraction observed. It consists of a large test-tube (T, Fig. 7) sealed into a wider tube, B, with which is connected a narrow tube, C, bent into a parallel branch, and terminating in a wider part, D. Into the upper part of D is passed a

fine, graduated tube, E, by means of a cork. By pushing the cork into D, mercury may be made to pass to any desired mark along E. The test-tube T is surrounded by air-free water, the remainder of B and the connecting tube C being filled with mercury. In using the apparatus it is completely surrounded by ice or snow in a large vessel, the temperature being thus reduced to 0°C . By bubbling air through ether placed in T, the water in contact with the tube is frozen. The ice produced will at first be below 0°C ., but on standing will attain the common temperature. The mercury is now made to reach a fixed point near the end of E, and the weighed substance dropped into T, which is then corked up. A certain amount of ice is melted, causing a contraction, which is measured by the altered position of the mercury in E. The result may be obtained by taking 1 c.c. of contraction to represent 12 grams of ice melted, a figure obtained by other experiments. If then the tube E be graduated in fractions of a cubic centimetre, the amount of contraction may be read off and translated into the corresponding weight. Thus a contraction of .25 c.c. would represent 3 grams of ice melted, requiring $3 \times 80 = 240$ calories, which are received from the substance dropped into T. The calculation is now identical with that used in Black's method. If, however, the tube E be graduated arbitrarily, the value in calories of a given contraction is obtained by pouring into T a weighed quantity of water at a known temperature, which on cooling to 0°C . would give out a known number of calories. Thus 5 grams of water at 20°C . would furnish 100 calories, from which the scale of E can be made to indicate calories evolved.

Example.—On placing 5 grams of water at 20°C . in a Bunsen calorimeter, the observed contraction was 30.8 scale divisions. On placing 20 grams of tin, also at 20°C ., in the instrument, a contraction of 6.95 divisions was observed.

$5 \times 20 = 100$ calories given out by water,

therefore

30.8 scale divisions = 100 calories,

and

6.95 scale divisions = 22.5 calories.

The specific heat of tin—that is, the number of calories given out by 1 gram falling 1°C . in temperature = $\frac{22.5}{20 \times 20} = .0562$.

Bunsen's calorimeter may be made to yield very accurate results, but owing to the necessity of keeping the apparatus continuously sur-

rounded by ice, is somewhat troublesome to use. The actual experiment, when the apparatus is ready, may be rapidly performed, and the specific heat of solids or liquids obtained with equal facility. The instrument, as will be shown later, may also be used to determine the latent heat of fusion of ice.

Condensation Method.—When steam at a given temperature condenses to form water at the same temperature, a definite quantity of heat is given out. Each gram of steam at 100°C. , on condensing to water at 100°C. , evolves 537 calories. Below 100°C. the number of calories given out is greater than 537, above, the number is less; being definite, however, at a given temperature. The condensation method, due to Dr. Joly, is based on this property of steam.

The apparatus consists of a sensitive balance, from one of the pans of which is hung a fine platinum wire, which is attached to the substance under experiment. The substance is surrounded by a jacket through which steam can be passed, the platinum wire by which the substance is held passing through a plaster of Paris stopper to the pan of the balance. The hole in the stopper must be large enough to allow the wire to hang freely, so that an accurate weighing is possible. The suspended substance is first weighed in air, and its temperature taken; after which steam is passed through the jacket for a short time, and the weight again taken. The increase in weight is due to water condensed on the surface of the solid, the amount condensed being that requisite to raise the temperature of the substance to that of the steam. The calculation is made from the equation—

$$\begin{aligned} &\text{Weight of substance} \times \text{specific heat} \times \text{rise in temp.} \\ &= (\text{weight of steam condensed} \times L) \end{aligned}$$

where L is the latent heat of steam at the temperature at which it is supplied to the jacket.

Example.—A piece of brass, weighing 50 grams in air, and at a temperature of 20°C. , was found to weigh 50.707 grams when surrounded by steam at 100°C.

The specific heat of brass is therefore

$$S = \frac{.707 \times 537}{50 \times (100 - 20)} = .095 \text{ nearly,}$$

since the weight of water condensed is $.707$ gram, and the latent heat of steam at 100°C. = 537 calories per gram.

If a large quantity of the substance be taken, more water may be condensed than is able to cling to the surface, and an error would

ensue from drops of water falling off. This difficulty is overcome by placing the specimen in a thin copper pan which is hung in the jacket from the platinum wire, and serves to collect any drops of water which may thus fall off. A blank experiment must be made to determine the weight of steam condensed by the copper pan and suspending wire, this weight being deducted from the total increase observed when the specimen is placed in the pan.

By using a metallic sphere, in which a quantity of gas could be compressed, Dr. Joly was able to obtain the specific heats of gases at *constant volume*. A blank experiment, with the sphere exhausted, gave the weight of steam condensed by the sphere itself, and on deducting this amount from the total obtained when the sphere was filled with compressed gas, the amount of condensation due to the gas was found, and the specific heat calculated in the usual way.

The condensation method furnishes an accurate means of determining the specific heat of a solid, and may also be used for liquids, which may be sealed up in a glass vessel of known thermal capacity and placed on the copper pan. In performing the experiment, the steam should be turned on rapidly, as otherwise there is a danger of drops condensing on the top of the jacket and falling on to the specimen or the copper pan.

Cooling Method.—If two substances, of equal dimensions and possessing the same kind of surface, be allowed to cool from the same temperature, the rate of cooling will be nearly proportional to the specific heats. Thus if two bars of metal of the same size be covered with lamp black, and allowed to cool in air from a temperature of 200° C., the time taken to fall through a given small range of temperature will be different in each case. Each bar, in the interval, loses an equal number of calories by radiation; but the loss of these calories will cause a different alteration in temperature owing to the bars possessing different specific heats. This may be used to *compare* the specific heat of two metals, but as the two bars will not be of equal weight, it is necessary also to take the specific gravity into account, as specific heats refer to equal weights. The procedure will be made clear from the following example:—

Example.—Two bars of equal dimensions, one of copper and the other of aluminium, were coated with lamp black and heated to 200° C. It was observed that the fall of temperature at the end of 1 minute on the copper bar was attained in 42 seconds by the aluminium bar. The relative specific heats, compared by *volume*, are

therefore as $\frac{60}{42} = \frac{10}{7}$. The copper bar, however, was heavier than

the aluminium bar in the ratio of their specific gravities, viz. $\frac{8.95}{2.65} = \frac{3.37}{1}$. Hence an aluminium bar equal in *weight* to the copper bar would have required (42×3.37) seconds to cool through the given interval. Hence

$$\frac{\text{Specific heat of copper}}{\text{Specific heat of aluminum}} = \frac{60}{42 \times 3.37} = \frac{1}{2.36},$$

or the specific heat of aluminium is 2.36 times that of copper.

The cooling method may also be applied to liquids, which are compared with water by observing the time required for equal volumes to cool through a given range of temperature. The liquid is placed in a small copper vessel coated with lamp black, and placed in a larger vessel furnished with an ice-jacket, to secure uniform conditions of cooling. Readings of temperature are taken by a thermometer placed in the liquid, and time observations are also made. The specific heats, for equal volumes, are proportional to the rate of cooling; and the specific heat of equal weight is obtained by dividing the volume result by the specific gravity of the liquid. Thus if the time taken by 100 c.c. of water to cool through a given interval is 1 minute, and for 100 c.c. of turpentine, through the same interval, is 24 seconds, the specific heat of the turpentine is to that of water as $\frac{24}{60} = .4$ by volume, and by weight $\frac{.4}{.87} = .46$, the specific gravity being .87.

The method of cooling may be made to yield fairly close results, but is not of such importance as the other methods.

Specific Heat of Gases.—The quantity of heat required to raise 1 gram of a gas by 1° C. depends upon the conditions existing during the application of the heat. If the gas be allowed to expand freely when heated, its pressure will remain constant, and the specific heat will have a certain value. If, on the other hand, the gas is contained in a closed vessel, and cannot expand, the pressure will increase when heat is applied, but the volume will remain constant, and the specific heat will be less than that obtained for the gas at constant pressure. These conditions would be fulfilled if the gas were contained in a cylinder fitted with a piston, which is allowed to move in the first case, allowing free expansion and maintaining constant pressure; but prevented from moving in the second case, thus maintaining constant volume. In the first case (constant pressure) the piston is forced along against the resistance offered by the atmosphere, and a certain amount of heat is converted into work to overcome the atmospheric

pressure, over and above that required to heat the gas. This extra amount of heat is not requisite in the second case (constant volume), consequently the heat expended is greater at constant pressure than at constant volume.

The specific heat of gases at constant pressure may be found by the method devised by Regnault, which is a modification of the method of mixtures. A known quantity of the gas is passed through a copper worm surrounded by boiling water, being thus heated to a known temperature. Immediately connected is a copper spiral surrounded by cold water in a calorimeter, through which the hot gas passes, escaping at the temperature of the water surrounding the spiral into the atmosphere. By this arrangement the gas is free to expand on heating, and consequently the experiment gives results at constant pressure. In calculating the result it must be observed that the temperature of the gas at the moment of escape into the atmosphere is not constant throughout, but rises as the temperature of the water in the calorimeter rises. In an experiment conducted uniformly, the average temperature of escape would lie midway between the initial and final, and this is assumed to be the case in the calculation.

Example.—When 60 grams of dry air, heated to 100°C. , are passed through a spiral surrounded by 200 grams of water at 20°C. , the final temperature of the water is observed to be 25°C. The water equivalent of the apparatus (calorimeter and spiral) is 20 grams. The average fall of temperature $= 100 - \left(\frac{20 + 25}{2} \right) = 77.5^{\circ}$. Calculating as usual,

$$60 \times S \times 77.5 = (200 + 20) (25 - 20),$$

whence

$$4650 S = 1100$$

and

$$S = .236.$$

The specific heat of a gas at constant volume may be obtained by Joly's steam calorimeter, as previously explained. As the air is not allowed to expand, owing to being enclosed in a sphere, the value obtained is the specific heat at constant volume.

For diatomic gases difficult to liquefy, the ratio of the two specific heats: that is, $\frac{\text{spec. heat at C.P.}}{\text{spec. heat at C.V.}}$, approximates to 1.4 in each case. For gases easily liquefied the ratio varies according to the gas, being, in general, less than 1.4. The ratio may be obtained by calculations on the velocity of sound, and by other means; and hence when the specific heat at constant pressure and the ratio are

known, the specific heat at constant volume may be calculated. It may be added that for monatomic gases (i.e. gases containing 1 atom in the molecule), such as argon and helium, the ratio of the specific heats is 1·6 to 1. The subject will be referred to again in Chapter VI.

Table of Specific Heats.—The specific heats of various substances, obtained by the methods described, are appended, the experimental temperatures also being given.

Name	Mean Specific Heat	Range of Temperature, °C.	Energy required to raise 1 gram 1° C. (ergs $\times 10^6$)
<i>Chemical Elements :—</i>			
		Between	
Aluminium . . .	·2122	15 and 97	8·91
Antimony . . .	·0486	13 „ 106	2·04
Bismuth . . .	·0298	9 „ 102	1·25
Cadmium . . .	·0548	0 „ 100	2·30
Copper . . .	·0933	15 „ 100	3·92
Gold . . .	·0316	0 „ 100	1·33
Iron . . .	·1124	0 „ 100	4·72
Lead . . .	·0315	19 „ 48	1·32
Mercury (liquid) . .	·0335	17 „ 48	1·41
„ (solid) . .	·0319	−70 „ −40	1·34
Nickel . . .	·1092	14 „ 97	4·59
Platinum . . .	·0323	0 „ 100	1·36
Silver . . .	·0559	0 „ 100	2·35
Tin (cast) . . .	·0559	0 „ 100	2·35
Zinc . . .	·0935	0 „ 100	3·93
<i>Other Solids :—</i>			
Glass . . .	·188 to ·198	15 „ 97	7·90 to 8·32
Brass . . .	·094	15 „ 100	3·95
German silver . . .	·094	200 „ 100	3·95
Ice . . .	·504	−20 „ 0	21·17
<i>Liquids :—</i>			
Alcohol (ethyl) . .	·615	at 30	25·83
Chloroform . . .	·235	„ 30	9·87
Ether . . .	·529	„ 0	22·22
Benzene . . .	·416	19 and 30	17·47
Sulphuric acid (conc.) .	·332	16 „ 20	13·94
„ (+ 5 H ₂ O) . .	·576	16 „ 20	24·19
Turpentine . . .	·454	at 40	19·07
<i>Gases :—</i>			
Air (const. press.) .	·237	10 and 100	9·95
Oxygen „ . .	·217	ditto	9·11
Nitrogen „ . .	·244	„	10·25
Carbon dioxide „ . .	·216	„	9·07
Ammonia „ . .	·508	„	21·34
Hydrogen „ . .	3·410	„	143·22

Name		Mean Specific Heat	Range of Temperature, °C.	Energy required to raise 1 gram 1° C. (ergs × 10 ⁶)
<i>Gases :—</i>				
By Joly's steam calorimeter	Air (const. vol.)	·172	{ Between 10 and 100 from 1 to 20 ats. press. 10 and 100 at 7 ats. press. 10 and 100 at 22 ats. press.	7·22
	Carbon dioxide (const. vol.)	·168		7·06
	" "	·174		7·31
<i>Vapours :—</i>				
Steam	(const. press.)	·480	100 and 120	20·16
Chloroform	"	·157	100 " 200	6·59
Ether	"	·487	70 " 200	20·45

Effect of Temperature on Specific Heat.—In general, the specific heat of a substance increases with the temperature. Thus, at 0° C. the specific heat of copper is ·0901; at 100° C. the value is ·0965. Taking the mean, the specific heat at 50° C. is ·0933, the increase with temperature being assumed to be uniform. The effect of temperature in the case of several substances is given by the following formulæ :

Copper	.	.	·0901 + ·0000648 t
Platinum	.	.	·0317 + ·000012 t
Silver	.	.	·0547 + ·000044 t
Iron	.	.	·1060 + 00014 t
Zinc	.	.	·0901 + ·000075 t

where t is the temperature in degrees Centigrade.

The specific heat of water has a minimum value at about 40° C., being greater at either higher or lower temperatures. If the value at 40° C. be called 1, the specific heat at 0° C. is 1·0110, and at 100° C., 1·0077. The value at 17·5° C. is 1·00263, which represents the mean specific heat deduced from the results obtained at different temperatures between 0° C. and 100° C. For this reason it is advisable to define the calorie as the amount of heat required to raise 1 gram of water from 17° C. to 18° C., as the extreme variations in value are less than if it be defined with respect to any other given degree. If the specific heat between 17° C. and 18° C. be called unity, the value at 0° C. is 1·0084, and at 100° C., 1·0050. The same figures represent the number of *average* calories (17° – 18°) required to raise 1 gram of water from 0° to 1°, and from 99° to 100° C. respectively.

Tilden has shown that at very low temperatures the specific heat of certain metals diminishes considerably. Thus nickel, which has a specific heat of $\cdot 1092$ between 20°C. and 100°C. , shows the value $\cdot 0838$ between -180°C. and 15°C.

Dulong and Petit's Law.—This law, as expressed by its discoverers, states that “the atoms of all elements have the same capacity for heat.” Or, in other words, if the specific heat of an element be multiplied by its atomic weight, the product will be the same for each element.

This law is not universally true if the specific heats are taken between the same range of temperature in each instance. In a large number of cases, however, the product (specific heat by atomic weight) is nearly constant, and approximates to $6\cdot 4$. For example, the atomic weight of mercury is 200, and the specific heat of the solid $\cdot 0319$, hence the product is $6\cdot 38$. Similarly, in the case of tin, atomic weight 118, specific heat $\cdot 0559$, the product is $6\cdot 6$. On the other hand, the product is only $5\cdot 4$ for sulphur, and $1\cdot 8$ for carbon; elements in general having an atomic weight of less than 30 showing a less product than $6\cdot 4$. The law is obeyed by most of the elements of atomic weight higher than 30, and is sufficiently general to be of assistance in deciding the atomic weight of a new element.

Effects of High and Low Specific Heats.—The fact that water possesses a higher specific heat than other liquids renders it the most efficient liquid to employ as a cooling agent in the condensers of steam-engines and in stills, and also in keeping down the temperature of the cylinders of internal combustion engines, and the barrels of machine-guns. Any other liquid would have to be used in greater quantity to produce the same cooling effect; and further advantages in favour of water are cheapness and non-inflammability. Hence, water is universally employed in all cases where a liquid cooling agent is required. The high specific heat of water is also responsible for the temperate character of insular climates, the surrounding water in the summer being for this reason at a lower temperature than the land, and in winter at a higher temperature; hence, winds from the ocean are relatively cool in summer and warm in winter, and extremes of heat and cold are prevented.

An example of the advantage of a low specific heat is furnished by steam-pipe coverings, as in this case, when starting from the cold, a low specific heat means a less absorption of heat by the covering in rising to its steady temperature.

CHAPTER IV.

EXPANSION.

Expansion of Bodies on Heating.—The general effect of a rise in temperature is to produce an increase in the dimensions of the heated body; and conversely, a decrease in temperature usually causes a shrinkage in size. There are, however, well-defined exceptions to the general rule. Water, on heating from 0° to 4° C. *contracts*; but above 4° C. expands. Water, in the liquid state, has therefore a minimum volume and consequently a maximum density, at 4° C. Indiarubber and silver iodide also contract on heating, and expand on cooling. A bar of iron or steel, on cooling from a high temperature, contracts uniformly to about 740° C., at which temperature it suddenly expands, the change, however, being accompanied by a rise in temperature. This phenomenon, discovered by Prof. Barrett, has been termed the “recalcescence” or re-heating of iron or steel, and is due to a molecular re-arrangement which causes heat energy to be disengaged. It is interesting to note that iron, which before recalcescence is non-magnetic, is powerfully attracted by a magnet immediately recalcescence has occurred, which is likewise true of steel. In the case of steel more than one recalcescence point may be noted, and a careful study of the phenomenon has led to important results in the treatment of steel when hardening and tempering. Recalcescence may be retarded by the presence of other metals in steel; and by alloying manganese with steel Hadfield has obtained manganese steels almost entirely non-magnetic. Barrett’s discovery was the starting-point of a series of most valuable researches on steel and its alloys, which have been carried out in recent years by M. Osmond, the late Sir W. Roberts-Austen, Hadfield, Arnold, and other workers. A number of the results obtained are recorded in the reports of the Alloys Research Committee of the Institution of Mechanical Engineers.

The amount by which most substances expand for a rise of 1° is very minute; but in spite of this fact due allowance for expansion or contraction is necessary in many engineering structures, and in

mechanisms. The force exerted by the substance, on expanding, is considerable; and if resisted might easily distort the expanding body, or any support to which it was rigidly attached. The actual force brought into play on expanding is equal to that required to extend the substance, mechanically, by the same amount. If, for example, an iron bar were heated from 0°C. to 100°C. , the increase in length is found to be $\cdot 0011$ cm. per centimetre of length. The force necessary to stretch a piece of iron 1 cm. long, and 1 sq. centimetre section, by $\cdot 0011$ cm., is equal to the weight of 2,000,000 grams. This figure therefore represents the expansive force exerted, and also the contractive force when the bar is cooled through the same range. The equivalent of this force in British units is a weight of nearly 2 tons; hence the obvious necessity of due allowance for free expansion in large girders, etc., which are subject to considerable variations in temperature.

Coefficient of Expansion.—In many cases, such as rules, measuring chains, rails, or bridges, the increase in *length* is the important factor, the expansion in other directions not being necessary to take into account. In measures of volume, such as a litre flask, and in the case of liquids, the increase in all directions must be considered. Increase in length is referred to as “linear” expansion, and increase in volume is termed “cubical” expansion. The amount by which a given substance expands is expressed in the form of a coefficient, which represents the increase in unit length (or volume) for a rise in temperature of 1°C. Hence

coefficient of linear expansion = increase in unit length for
a rise of 1°C.

$$\text{or,} \quad = \frac{\text{increase in length on being raised } t^{\circ}}{\text{original length} \times t^{\circ}}.$$

In dealing with cubical expansion, the word “volume” is substituted for “length.” Occasionally it is necessary to know the increase in area only, as in the case of a thin plate, in which instance the word “area” may be inserted. Problems involving superficial expansion only, however, seldom occur in practice.

The coefficient of linear expansion of solids is always a small figure; that of iron being $\cdot 0000117$, and of aluminium, $\cdot 0000222$. Owing to the small value, the coefficient of cubical expansion is approximately equal to 3 times the linear. For if a cube of 1 cm. side be taken, and raised in temperature by 1°C. , each side will increase in length by a small amount, α , which represents the coefficient of

linear expansion. Hence the volume of the cube would become $(1 + a)^3 = 1 + 3a + 3a^2 + a^3$. As a is a minute fraction, its square and cube will be excessively small, and terms involving them may be ignored. Hence the new volume $= 1 + 3a$, as nearly as possible. But the original volume $= 1$ c.c.; hence the cubical expansion of unit volume for $1^\circ =$ coefficient of cubical expansion $= 3a$ or linear coefficient.

Determination of the Linear Expansion of Solids.—In determining the coefficient of linear expansion of solids, a rod of the substance is taken and its length measured accurately at a known temperature, t° . It is then heated to a known higher temperature, t_1° , and the increase in length measured by a micrometer, spherometer, vernier microscope, a train of levers, or optical means. If $K =$ the increase in length, and l the length at t° , the coefficient a , is determined by the equation—

$$a = \frac{K}{l \times (t_1 - t)}.$$

Example.—If the length of a bar $= 60$ cm. at 10°C. , and increases in length by $.108$ cm. when heated to 100°C. , the coefficient of linear expansion $= \frac{.108}{60 \times (100 - 10)} = .00002$. For each centimetre increases in length by $\frac{1}{8000}$ of the total increase for 90° rise in temperature; hence 1 cm. increases in length by $\frac{1}{8000}$ of the total for a rise of 1°C.

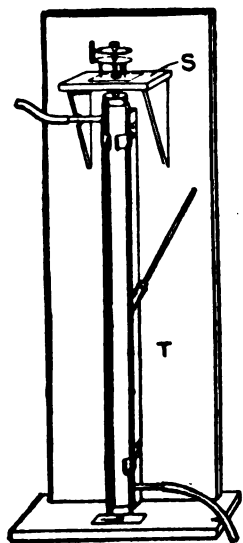


FIG. 8.—DETERMINATION OF THE COEFFICIENT OF EXPANSION OF SOLIDS.

Instruments based on each of the above methods of measuring the exact elongation of a bar are in use. A simple form, involving the use of a spherometer, is illustrated in Fig. 8. The rod is enclosed in a brass tube, T , which is fastened vertically to a stand. The lower extremity of the rod passes through a cork in the end of the tube, and rests on a glass plate sunk into the base of the apparatus. The upper end of the rod is passed through a cork at the top of the tube, and is free to move vertically. The spherometer stands on a piece of plate glass held on the shelf, S , a hole being drilled in the glass to admit of the central support of the spherometer being

screwed down so as to touch the rod. In commencing the experiment cold water is run through the tube until the temperature is steady, when the screw is rotated until the central support of the spherometer just touches the bar. The temperature and reading of the spherometer are now taken, and steam allowed to pass through the tube for a few minutes. The spherometer screw is now raised until it again just touches the top of the rod, when the reading is again taken. The difference between this and the previous reading gives the elongation of the rod between the starting temperature and that of the steam. The length of the rod when cold is measured with a metre rule; a suitable length for the experiment being 70 cm. If the spherometer screw possesses 20 threads per cm., and the graduated plate be divided into 100 equal parts, the elongation may be measured to $\frac{1}{2000}$ part of a centimetre, or .005 cm.

In another form of apparatus a horizontal bar of the substance is clamped at one end, the other end being free to move in a groove. A micrometer screw is made to touch the free end when cold, and afterwards when hot, the elongation of the bar being the difference between the readings. The bar is heated by steam circulating in a metal tube enclosing the bar.

A third method consists in making two fine marks on a rod or bar of the substance, and measuring the distance between them when cold. The bar is then placed in a water-bath, and a vernier microscope focused over each mark. The water in the bath is then boiled, and after a few minutes the microscopes are moved horizontally by means of a screw until the cross-wire of each microscope is again over the mark on either end of the bar. The distance moved by each microscope is read off on the scale; the two distances added together give the total increase in length. Roy and Ramsden's method is a refinement of this mode of procedure.

The plan adopted by Laplace and Lavoisier is illustrated in Fig. 9. A rod of the material rests on rollers in a trough, and may be heated by boiling water in the trough. One end of the bar is in contact with the side of the trough, whilst the other end presses against a lever. A telescope is pivoted at O so as to be capable of moving in a vertical plane. At the commencement of the experiment the telescope is horizontal, and is focused on a scale, S, placed at a known distance, the division on the scale covered by the cross-wire on the telescope being noted. The water in the trough is now boiled causing the bar to expand. The lever L, and the attached telescope are thereby made to take up a new position, indicated by the dotted lines. On looking through the telescope the cross-wire will now

appear over another mark B on the scale. The amount C D, by which the bar has elongated, is obtained from the ratio $\frac{C D}{A B} = \frac{O C}{O A}$, as O C D and O A B are similar triangles, in which the lengths of the sides O A, A B, and O C are known. The coefficient is obtained, as usual, by dividing the observed elongation by the original length and rise of temperature. It is evident that the distance between A and B will depend upon the distance of the scale from the centre of the telescope; and by placing the scale a number of feet away a very small increase in length may be observed.

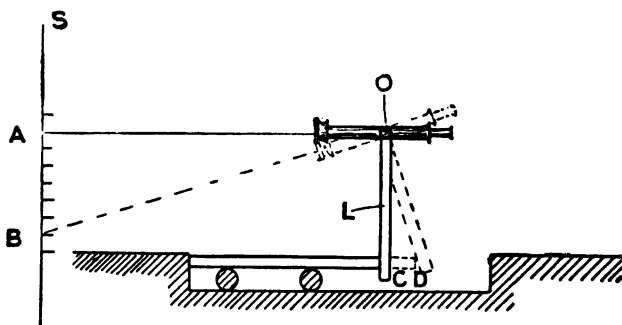


FIG. 9.—LAPLACE AND LAVOISIER'S APPARATUS FOR DETERMINING THE LINEAR EXPANSION OF SOLIDS.

Many forms of apparatus exist in which the elongation is measured by a suitable train of levers for multiplying the movement of the bar or rod experimented on, the effect being increased in some cases by attaching a mirror to the end lever, and observing the movement of a spot of light reflected from the mirror on to a scale placed at a known distance.

The results obtained by one or other of the above methods are appended. The amount of expansion for 1° F. is $\frac{5}{9}$ of that occurring for a rise of 1° C. The figures in column 3 are therefore $\frac{5}{9}$ of the corresponding figure in column 2.

The values given in the following table represent the average coefficient between 0° and 100° C. At higher or lower temperatures the value may vary considerably. The mean coefficient for iron, as shown in the table, is $\cdot 0000117$; but between 0° and 1000° C. the mean value rises to $\cdot 000015$. When values at high or very low temperatures are required, special experiments must be made.

Of the substances enumerated, ebonite possesses the highest co-

COEFFICIENTS OF LINEAR EXPANSION OF SOLIDS
BETWEEN 0° C. AND 100° C.

Substance	Coefficient of Expansion per Degree Centigrade	Coefficient of Expansion per Degree Fahrenheit
Zinc	·0000292	·0000162
Aluminium	·0000222	·0000123
Silver	·0000194	·0000108
Brass	·0000189	·0000105
Copper	·0000168	·0000093
Gold	·0000144	·0000080
Iron	·0000117	·0000065
Steel (mild)	·0000110	·0000061
Platinum	·0000089	·00000494
Glass (average)	·0000087	·00000483
Nickel-steel alloy (36 per cent. nickel)	·0000087	·00000483
Platinum-iridium alloy (10 per cent. iridium) }	·00000884	·00000491
Granite	·00000868	·00000482
Sandstone	·0000117	·0000065
Sulphur	·0000641	·0000356
Slate	·0000104	·00000578
Marble (white)	·0000107	·00000594
Porcelain	·0000045	·0000025
Brick	·0000055	·00000306
Deal (white)	·0000046	·00000255
Ebonite	·0000770	·0000428
Lead	·0000280	·00001555
Pure vitrified silica (up to 1000° C.) .	·00000059	·00000033
Jena thermometer glass	·0000080	·0000044
Ice (between - 27° C. and - 1° C.).	·0000524	·0000291

efficient, which is 7 times that of steel. Sulphur has also a high value, and amongst metals zinc and lead have the highest values. The figure for platinum is very low, and almost corresponds with that of glass. The various kinds of glass, however, differ considerably in respect to amount of expansion, but it is possible to produce glass possessing a coefficient practically identical with that of platinum. In such glass platinum wire may be sealed so as to form a vacuum-tight

joint, and without danger of cracking owing to unequal expansion. This property is taken advantage of in the manufacture of electric lamps, the interiors of which are exhausted of air, and the current furnished to the carbon or metal filament through platinum wires sealed through the glass. Platinum is similarly used for the electrodes of vacuum tubes, and for all cases where it is desired to obtain an electric discharge between two points in the interior of a sealed glass vessel. Ordinary soda or lead glass do not always possess a coefficient identical with platinum, and often crack on cooling after sealing-in a platinum wire. A special enamel of correct coefficient may be purchased, however, which on heating will incorporate with the glass. In sealing a platinum wire into ordinary glass, therefore, it is best to blow a small hole at the desired spot and place a collar of enamel round the hole, so as nearly to close it. The wire is then pushed through, and heat applied until the enamel has thoroughly melted round the wire and into the glass in the vicinity. The joint should then be gently blown so as to prevent any undue thickness of material at any part, and will then be found durable. The sealing of platinum into glass hermetically is probably due not only to identity of expansion, but also, in part, to the absence of oxidation on the surface of the platinum. It is possible to prepare alloys of nickel and steel possessing a coefficient of expansion identical with that of glass, and there appears to be no good reason, other than possible oxidation, why such an alloy could not be obtained which would replace platinum in electric lamps, etc., resulting in a great saving in the cost of manufacture.

The extremely low coefficient of nickel-steel, containing 36 per cent. of nickel, is of considerable interest and importance. The value is only $\frac{1}{10}$ that of glass, and is so small that 1 mile of wire or rod made of this material would only increase in length by a little more than $\frac{1}{2}$ an inch on being raised by 10° C. The low expansion of this and other nickel-steel alloys was discovered by M. Guilleme, who found that the value given in the table is not attained immediately, as is the case with ordinary metals. If the temperature were raised by some small amount—say from 10° to 30° C.—the material would have to be retained at the latter temperature for two months before expanding by the amount indicated by the coefficient. During this period a gradual increase in length would take place, finally attaining a maximum represented by the figure in the table. It therefore follows that a bar of the alloy, subjected to ordinary fluctuations of temperature in the atmosphere, would remain as nearly as possible constant in length. This alloy, which does not easily rust, is now

being applied to the manufacture of standard measures of length and volume, for the pendulums of clocks, and other uses.

Use of Coefficients of Linear Expansion.—A few examples are given showing the method of employing the coefficient of expansion in calculations. It is not necessary, in general, to change British units into metric, or *vice versa*; and if temperatures are expressed in Fahrenheit degrees the coefficient per degree Fahrenheit is used. It must be remembered that the coefficient expresses the increase of unit length for 1° in terms of that unit, thus

- 1 cm. of brass increases by $\cdot 0000189$ cm. for a rise of 1° C.,
 or
 1 foot of brass increases by $\cdot 0000189$ ft. for a rise of 1° C.,
 or
 1 mile of brass increases by $\cdot 0000189$ mile for a rise of 1° C.

The increase is therefore always expressed in the same unit as that chosen for the original length.

Example.—(a) A brass scale, exactly 1 metre long at 15° C., is at a temperature of 35° C. At this temperature the length will be $1 + (\cdot 0000189 \times 20)$ metre = $1\cdot 00038$ metre (approx.) or $100\cdot 038$ centimetres.

A nickel-steel scale, under the same conditions, would have a length of $1 + (\cdot 00000087 \times 20)$ metre = $1\cdot 0000174$ metre or $100\cdot 00174$ centimetres, if it had been kept at 35° C. for two months. Or, if 1 yard long at 15° C., the length at 35° C. would only increase by $\cdot 00063$ of an inch.

Example.—(b) A steel chain, 66 feet long, as used for surveying, if correct at 60° F., would have a length at 32° F. of

$$66 - (\cdot 0000061 \times 28 \times 66) \text{ feet} = 65\cdot 989 \text{ feet (approx.)}$$

(Note that as 1 foot contracts by $\cdot 0000061$ foot for a fall of 1° F., the total contraction per $^{\circ}$ F. will be $66 \times \cdot 0000061$ foot.)

The contraction is about $\frac{1}{8}$ of an inch, and the error in measuring 1 mile under the conditions would be 10 inches.

Example.—(c) A glass measure, of capacity 1000 cubic centimetres at 15° C., would at 45° C. possess a capacity of $1000 + (1000 \times \cdot 0000087 \times 3 \times 30)$ c.c. = $1000\cdot 783$ c.c.

(The cubical expansion is 3 times the linear, and as the vessel expands in every direction it will possess the same external dimensions as if it were a solid piece of glass.)

A brass gallon measure, under the same conditions, would increase in capacity by

$$(\cdot 0000189 \times 3 \times 30) \text{ gallon} = \cdot 0017 \text{ gallon, or about } \frac{1}{580} \text{ of a gallon.}$$

Expansion of Liquids and Gases.—A measured volume of a liquid or gas must be contained in a vessel or envelope, and on raising the temperature the vessel, as well as its contents, will expand. Liquids, in general, have a higher coefficient of expansion than solids; hence if a vessel be filled with a liquid, and heated, a quantity of the liquid will overflow. If vessel and liquid expanded by the same amount, no overflow would take place. Any measurement of the expansion of liquids from the amount expelled from a vessel on raising the temperature by a given amount, is therefore only relative, and different values would be obtained with vessels of different materials. The value is always less than the true expansion, as owing to the increase in size of the vessel some of the liquid is retained, which would be expelled if the vessel could be prevented from expanding. The true expansion is evidently the sum of the amount expelled and the amount by which the vessel has expanded. The same argument holds true for gases; but as gases have a very high coefficient of expansion, the increase in size of the vessel is very small by comparison.

It is customary, in the cases of gases and liquids, to express the coefficient of expansion in terms of the volume occupied at 0°C . or 32°F . Hence the coefficient of expansion of a liquid or gas may be defined as "that fraction of its volume at 0°C . by which it increases on being raised in temperature by 1°C ." Or, when Fahrenheit degrees are used, "that fraction of its volume at 32°F . by which it increases for a rise in temperature of 1°F ." Many advantages are gained, particularly in the case of gases, by defining the coefficient with respect to this special temperature.

Determination of the Coefficients of Expansion of Liquids.—The methods which may be adopted for obtaining the coefficients of expansion of liquids are: (1) The *weight thermometer* method, in which the weight expelled from a full vessel, containing a weighed quantity of the liquid, is observed for a given rise of temperature. (2) By measuring the increase in volume in a graduated tube of a known volume of the liquid. (3) By observing the specific gravity of the liquid at different temperatures. (4) By Dulong and Petit's hydrostatic method, which gives the real expansion directly, without in-

volving any correction for the expansion of the containing vessel. A description of each will now be given.

Weight Thermometer Method.—A vessel furnished with a capillary outlet—such as a 25 c.c. specific gravity bottle with a bored stopper—is filled with the liquid at 0°C . by surrounding with ice, and, when cold, inserting the stopper. The bottle is now weighed, and placed in a bath of water at a known, constant temperature. When no further outflow of liquid through the bore of the stopper is observed the bottle is removed, dried on the exterior, and again weighed. The decrease in weight gives the amount of liquid expelled, and this represents the expansion due not to the quantity of liquid originally present, but to the liquid remaining in the bottle. For, if the residual liquid be heated from 0° to the higher temperature, it will expand so as just to fill the bottle. Hence the expelled liquid, which would fill the vacant space in the bottle, measures the expansion of the liquid left in. Taking weights as proportional to volumes, the relative expansion of the liquid is given by the equation—

$$\alpha = \frac{W - W_1}{W_1 (t_1 - t)}$$

where

W = original weight of the liquid present,

W_1 = weight of remaining liquid,

t_1 = temperature to which liquid is heated,

t = initial temperature = 0°C .

The figure obtained, however, will only be the relative or apparent coefficient; that is, the amount by which 1 cubic centimetre or 1 unit volume expands for 1°C ., minus the amount by which a glass vessel of 1 cubic centimetre capacity expands for 1°C . If the latter be known, and be added to the apparent expansion of the liquid, the real or absolute coefficient is obtained. Or,

Coefficient of real expansion = (coefficient of apparent or relative expansion + coefficient of cubical expansion of material of vessel).

Example.—A glass vessel weighs 50 grams when empty, and 710 grams when full of mercury at 0°C . On heating to 100°C ., 10 grams are expelled. Hence the coefficient of apparent expansion =

$$\frac{\text{weight expelled}}{\text{residual weight} \times \text{rise of temp.}} = \frac{10}{650 \times 100} = .000154.$$

Since the cubical coefficient for glass is $\cdot 000026$, the real expansion coefficient = $(\cdot 000154 + \cdot 000026) = \cdot 00018$.

(Note that the total residual weight is 700 grams, of which 50 are due to the vessel.)

The value obtained by the weight thermometer is, of course, the average coefficient between the temperatures employed.

Coefficients of Expansion of Liquids from Measurement of Increased Volume.—In this method, due

to Pierre, the liquid is placed in a bulb of known capacity, to which is attached a graduated tube. The volume of the bulb must be known in terms of the graduations on the tube. The volume of the liquid is read when the bulb is placed in ice, and again when immersed in a bath at temperature t_1 . The coefficient of apparent expansion will then be given by the equation

$$\alpha = \frac{V_1 - V}{V(t_1 - t)}$$

where

V = original volume, at $^{\circ}\text{C}.$,

V_1 = increased „ at $t_1^{\circ}\text{C}.$

t = original temperature = $0^{\circ}\text{C}.$

t_1 = temperature to which liquid is heated.

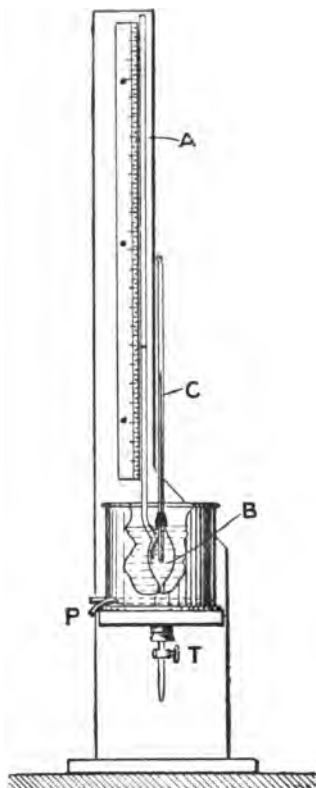


FIG. 10.—YOUNG AND DARLING'S APPARATUS FOR DETERMINING THE COEFFICIENT OF EXPANSION OF LIQUIDS.

If a glass bulb be used, the real expansion is obtained by adding $\cdot 000026$ to the apparent coefficient.

An improved form of apparatus for this purpose has been devised by J. Young and the author, and is illustrated in Fig. 10. A bulb of about 25 c.c. capacity, B, is connected to a piece of capillary tubing furnished with a tap, T, at the lower end, and to a graduated tube, A, about 50 cm. long at the top. A thermometer, C, passes through a tight joint into the centre of the bulb; and the instrument

is fixed in a bath, which may be heated by passing steam through the pipe, P. The liquid is drawn up into the bulb by placing the end of the tube below the tap in a beaker containing the liquid, and applying suction at the end of the tube A, to which a piece of india-rubber tubing is attached for the purpose. When bulb and graduated tube are full, the tap is closed, and the bath filled with ice. When a temperature of 0°C. has been attained, the tap is carefully opened so as to allow the column of liquid in A to fall to the zero mark. The ice is now removed, and the bath filled with water, which is then raised to any desired temperature by passing steam through the pipe, P. The thermometer and position of the liquid in A are read when, on constant stirring, both readings are steady. Readings may be taken every 10° , and the expansion at different temperatures thus measured. The apparent coefficient may be calculated as before, the volume, V, of the bulb up to the zero mark being ascertained by filling with mercury at 0°C. , which is then run out and weighed; the capacity of the tube being similarly found. When this has been carefully done, a constant may be found from which the coefficient can be obtained from the number of divisions through which the liquid expands for a given rise of temperature.

Example.—In an apparatus made as described, the capacity of the bulb up to the zero mark was 25.2 cubic centimetres; and each division of the graduated tube corresponded to $.0305$ of a cubic centimetre. When turpentine was allowed to expand from 0° to 50°C. , the column of liquid in the graduated tube reached the position indicated by 40.1 divisions. Hence the increase in volume (apparent) is $40.1 \times .0305$ cubic centimetres, and the coefficient $= \frac{40.1 \times .0305}{25.2 \times 50} = .00097$. Adding the cubical coefficient of glass, $.000026$, the real coefficient for turpentine is $.000996$, or practically $.001$.

The values $.0305$ and 25.2 are constant, and if a number of liquids be compared over the same range, t will also be constant in the expression

$$a = \frac{n \times g}{b \times t}$$

where n is the number of divisions through which the liquid expands; g the capacity of 1 division of the tube; b the capacity of the bulb; and t the temperature when the starting temperature is zero or 0°C.

The value of $\frac{g}{b \times t}$ can be calculated, and the figure obtained will, on multiplying by n , give the coefficient for any liquid between 0°

and $t^{\circ}\text{C.}$ Taking $t = 50^{\circ}\text{C.}$, as in the previous example, the value of $\frac{g}{b \times t}$ is $\frac{.0305}{25.2 \times 50} = .0000242$. If a liquid expanded through 20 divisions for a rise of temperature from 0° to 50°C. , a would equal $20 \times .0000242 = .000484$. Or for this range, $a = \pi \times .0000242$.

The advantage of the apparatus described is that the liquid may be run out and replaced by another, which is practically impossible with a closed bulb. The labour involved in calibrating and filling a fresh bulb for each liquid is thus saved. The simplicity of the calculation, and the ease with which the expansions may be tested over different ranges of temperature, are further advantages.

Coefficient of Expansion of Liquids from Specific Gravity.—When a liquid expands its density diminishes. If 10 cubic centimetres of a liquid expanded to 10.5 cubic centimetres, the density would only be $\frac{100}{105}$ or $\frac{20}{21}$ of its former value; or, in general, the density varies inversely as the volume occupied. By determining the specific gravity of a liquid at different temperatures it is therefore possible to infer the increase in volume, and hence to calculate the coefficient of expansion. The specific gravity may be determined by weighing a glass stopper in the liquid at 0°C. and at some higher temperature, the volume of the glass stopper at 0°C. having been previously found. The calculation of the result is obtained as in the following example.

Example.—A glass stopper has a volume of 4 cubic centimetres at 0° , and weighs 10 grams in air. When suspended in a liquid at 0°C. , it weighs 6.8 grams. Hence the weight of the displaced liquid is $(10 - 6.8) = 3.2$ grams; and as the volume displaced is 4 c.c., the specific gravity of the liquid is $\frac{3.2}{4} = .8$ at 0°C. At 80°C. the stopper, when immersed in the liquid, weighs 7.033 grams. The weight of liquid displaced $= (10 - 7.033) = 2.967$ grams. The volume of the displaced liquid is equal to that of the stopper at 80°C. , that is, $4 + (4 \times .000026 \times 80)$ c.c., $= 4.0083$ c.c. Hence the specific gravity of the liquid at $80^{\circ} = \frac{2.967}{4.0083} = .74$.

But

$$\frac{\text{volume at } 80^{\circ}}{\text{volume at } 0^{\circ}} = \frac{.80}{.74};$$

\therefore

$$1 \text{ c.c. at } 0^{\circ}\text{C. will occupy } \frac{80}{74} = 1.081 \text{ c.c.}$$

Hence

$$a = \frac{\text{increase for 1 c.c. at } 0^{\circ}\text{C.}}{\text{rise of temperature}} = \frac{.081}{80} = .001025.$$

The result will be the absolute coefficient, as the expansion of the glass stopper was allowed for. The method possesses the two drawbacks of difficulty of maintaining a constant temperature during weighing, and the necessity of a complicated calculation to obtain the result.

Dulong and Petit's Hydrostatic Method.—This method was devised by Dulong and Petit for the purpose of obtaining accurately the coefficient of real expansion of mercury, a knowledge of which is necessary for many purposes, such as correcting the height of the barometer for temperature, and also the height of mercury columns in general. The result obtained is independent of the size or material of the vessels used, and therefore gives the real or absolute expansion. The method is based on the principle that when two liquids, of different densities, are in equilibrium in a U-tube, the heights above the common level vary inversely as the densities, and are the same whatever the diameter of either tube. Thus if mercury be present in one limb, and water in the other, the vertical heights, measured from the line of contact, will be as 1 to 13.6, or inversely as the densities. If a single liquid be present in the U-tube, and one limb be heated whilst the other is kept cold, the hot portion of the liquid will expand and fall off in density. When in equilibrium, however, the heights must be inversely as the densities, irrespective of the expansion of the tube; and if these two heights be accurately measured, the alteration in density, and from it the coefficient of real expansion, may be determined.

Example.—The water in the gauge-glass of a boiler is at the same level as the water in the boiler, when both are at the same temperature. When steam is being produced, the level in the gauge-glass is slightly lower than that in the boiler, as the water it contains is colder and therefore denser. The water in the boiler may have an area many thousand times that of the gauge-glass, but this makes no difference to the respective levels.

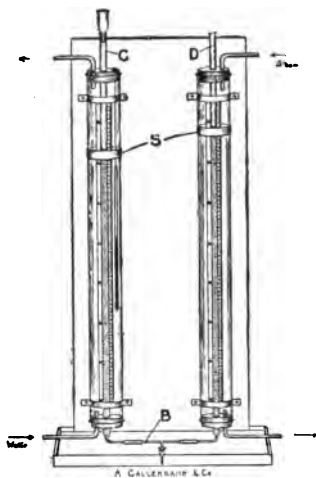


FIG. II.—APPARATUS FOR DETERMINING THE ABSOLUTE EXPANSION OF LIQUIDS.

The apparatus depicted in Fig. 11 illustrates the manner in which Dulong and Petit's method may be carried out experimentally. It consists of a U-tube C D, of which the separate limbs are connected by a capillary tube, B, which, whilst allowing a free transference of pressure between the two limbs, prevents any appreciable transfer of heat by conduction or convection from one limb to the other. Each limb of the U-tube is surrounded by a jacket, that surrounding C containing ice or cold water, whilst that surrounding D is fitted, so that steam from a boiler may be passed through. The heights of the separate columns of liquid may be measured from the metre scale by means of sliders, S, moving over the scale. The zero of the metre scale is placed opposite the centre of the capillary connection, which represents the common level, and the heights are read off when, on passing steam freely, the levels are observed to be constant. The heights may be measured more accurately, if desired, by the aid of a cathetometer. The result is calculated as under :—

Let h_0 = height of column surrounded by ice ; d its density ;
 h_i = " " steam ; d_1 "

Then from the hydrostatic principle that heights vary inversely as the densities,

$$h_0 \times d = h_i \times d_1 \quad . \quad . \quad . \quad (1)$$

or

$$(\text{lesser height} \times \text{greater density}) = (\text{greater height} \times \text{lesser density}).$$

The density, d_1 , depends on the amount by which the liquid has expanded. Let a = the coefficient of real expansion ; then 1 c.c. on heating from 0° to t° would possess a volume of $1 + a t$ c.c., and its density will be less in the ratio $\frac{1}{1 + a t}$.

Hence

$$\frac{\text{Density at } 0^\circ}{\text{Density at } t^\circ} = \frac{1 + a t}{1},$$

or

$$d = d_1 (1 + a t).$$

Substituting in (1), we have,

$$h_0 \times d_1 (1 + a t) = h_i \times d_1$$

\therefore

$$h_0 (1 + a t) = h_i$$

and

$$\alpha = \frac{h_t - h_0}{h_0 t}.$$

This value is independent of the expansion of the hot limb, which, although causing an increase in diameter, does not affect the results obtained from the final measurements. During the experiment, while the hot limb is rising in temperature, the expansion increases the diameter and tends to make the hot liquid fall below its correct level. A slight flow of liquid from the cold tube, however, causes the columns to maintain equilibrium, and thus compensates for the expansion. Hence the height of the cold column falls slightly until the hot column attains the temperature of the steam, and its height must be measured at the end of the experiment.

Example.—The following values were obtained with mercury: Height of column surrounded by ice = 91.2 centimetres; of hot column at 100° C. = 92.85 cm. Hence

$$\alpha = \frac{92.85 - 91.2}{91.2 \times 100} = .000181 \text{ nearly.}$$

When cold water is used instead of ice, the expression $(t_1 - t_2)$ must be used in the formula instead of t ; t_1 representing the temperature of the steam, and t_2 that of the cold water.

In Regnault's modification of the apparatus, the capillary connection is near the top of the U tube, being sealed across. Convection currents of the hot liquid, if existing, would merely float on the top of the cold column, and not penetrate its mass. The tubes are brought into parallel branches at the lower end, and connected by a T piece into which air is forced to maintain the weight of the columns. The difference of level is read off from the parallel branches, and the lengths measured from the centre of the capillary tube to the top of the respective columns. This inverted arrangement ensures the absence of errors due to convection.

The coefficients of expansion of several liquids are given in the accompanying table, the figures representing the mean values between the stated temperatures. The mean value for water between 15° C. and 100° C. is included, but owing to the exceptional character of the expansion at different temperatures, special mention will be made of the volume changes observed with this liquid.

Mercury, which possesses the lowest coefficient, expands by almost

F

COEFFICIENTS OF EXPANSION OF LIQUIDS.

Substance and Range	Apparent or Relative Expansion in Glass		Real Expansion = (Relative + '000026) per °C.	
	Per Degree C.	Per Degree F.	Per Degree C.	Per Degree F.
Mercury 0° and 100° C.	'000155	'0000855	'000181	'0001005
Alcohol 0 „ 40	'00111	'000617	'001136	'000630
„ 0 „ 1	'00102	'00057	'001046	'000581
Ether 0 „ 33	'00210	'00117	'002126	'001181
Benzene 11 „ 80	'00138	'000766	'001406	'000781
Turpentine 0 „ 100	'001024	'00057	'001050	'000583
Water 15 „ 100	'00045	'00025	'000476	'000264

exactly the same amount at any range of temperature between 0° and 100° C.; and this is one reason why mercury is selected for use in thermometers. Alcohol, and other liquids generally, have a higher coefficient at higher ranges. Turpentine probably stands next to mercury in respect to the uniformity of its expansion. The special case of water will now be considered.

Expansion of Water.—In order to observe the peculiarities connected with the expansion of water, the apparatus of Young and the author, illustrated in Fig. 10, is well suited. Commencing at 0° C., by surrounding the bulb with ice, it will be observed that on warming the water at first contracts slightly, until the temperature indicated is between 5° and 6° C. On further heating expansion takes place, and if the amount of expansion be taken at equal intervals—say every 5°—it will be observed to increase progressively. Between 90° and 95° C. the amount of expansion will be observed to be several times greater than that noted between 10° and 15°. In order better to observe the change of volume near the freezing point, the graduated tube should possess a very fine bore, and the observation started at about 15° C., the graduated tube being nearly filled. The temperature is then gradually lowered by adding ice to the water in the bath, and the stationary readings of the column and thermometer taken. A progressive contraction will be noticed until the temperature is about 5·5° C., and below this temperature the column will be observed gradually to rise until 0° is reached.

It must not be assumed from this experiment that the minimum volume of the water is attained at 5·5° C., for the glass vessel is also contracting. The shrinkage of the vessel, however, is uniform, and

the experiment indicates that at 5.5°C . the water and glass contract by equal amounts, and hence the column is stationary. Below this temperature the glass contracts more than the water, until 4°C . is reached, hence the liquid is slightly squeezed up the column. After 4°C . down to 0° , the water expands and rises in the column, the effect being increased by the continued shrinking of the glass bulb. In order to prove that the volume is a minimum at 4°C ., it is obviously necessary to have some means of eliminating the effects due to the contraction of the vessel. This may be done, experimentally, by placing in the bulb $\frac{1}{7}$ of its volume of mercury. When

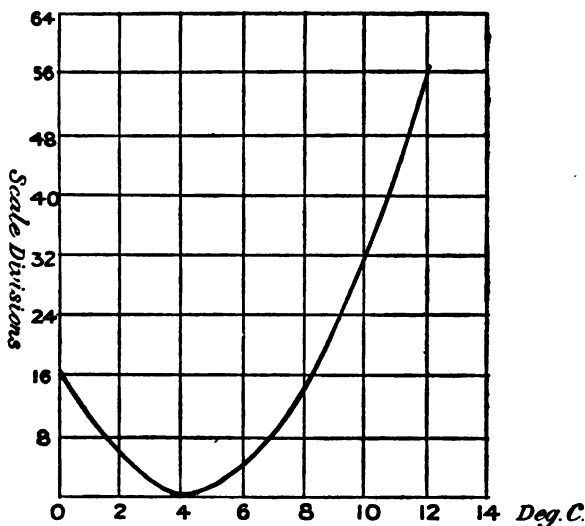


FIG. 12.—CURVE SHOWING THE VOLUME CHANGES OF WATER BETWEEN 0°C . and 12°C .

the glass shrinks, thus tending to raise the column, the mercury will shrink by an equal amount, and thus prevent the column from rising from any cause other than the expansion of the water. The true variations in the volume of the water will then be observed, and the minimum will be found to occur at 4°C . The reason why $\frac{1}{7}$ of the volume of the bulb is filled with mercury, is that the coefficients of expansion of glass (cubical) and mercury are in the ratio of 1 to 7. Hence $\frac{1}{7}$ of a c.c. of mercury will compensate for the expansion of 1 c.c. of the glass vessel.

The results of an experiment with this apparatus, containing $\frac{1}{7}$ of its volume of mercury, are shown graphically in Fig. 12, in which

scale divisions on the tube are plotted against temperatures. The lowest position of the column is called zero, and the following are the observations from which the curve is drawn :—

	Temperature, °C.	Height of Column	
	0	16 divisions	
	2	6 "	
	4	0 "	
	6	3·5 "	
	8	14 "	
	10	31·5 "	
	12	56 "	

The curve is not symmetrical on either side of the 4° ordinate, as the volume at 2° is equal to that at 6·6°, and at 0° equal to that at 8·3°.

The temperature of minimum volume is also that of maximum density, and has been chosen as the standard temperature for the unit of mass—the gram—which is the mass of 1 cubic centimetre of water at 4° C.

The temperature of maximum density is lowered by the presence of dissolved salts in water. Thus an 8 per cent. solution of common salt has a maximum density at $-16\cdot6^{\circ}$ C. Moreover, the expansion of the solution at higher temperatures is much more uniform than that of pure water. The author has found that strong saline solutions in general have a slightly higher average coefficient of expansion than water between 10° and 85° C., and expand more regularly.

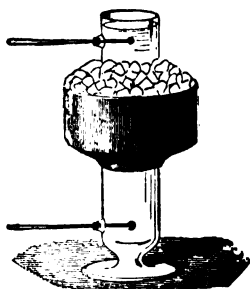


FIG. 13.
HOPE'S APPARATUS.

The temperature of maximum density of water may be found by Hope's apparatus, Fig. 13. A cylinder containing water is surrounded by a gallery in which a freezing mixture is placed. Two thermometers are inserted in the water, one near the surface, and the other near the bottom of the cylinder. Soon after the freezing mixture is placed in the gallery, the lower thermometer will indicate

a fall of temperature, whilst the upper one will be unaffected for some time. Finally, the lower thermometer will remain stationary at 4°C. , whilst the temperature indicated at the top may fall to zero, and the upper water may finally freeze. The explanation of these observations is that the water opposite the freezing mixture, on being slightly cooled, sinks owing to the attainment of a greater density by contraction. The warmer water below is displaced upwards and also cooled, and this circulation continues until the main mass of the liquid attains a temperature of 4°C. A further cooling causes expansion, and therefore loss of density; hence the water below 4°C. will rise, and the upper portion will be frozen if the freezing mixture be sufficiently powerful. The temperature at which the convection currents cease to sink is obviously that at which the density is a maximum.

The freezing of a pond of water on the surface only is due to the maximum density occurring above the freezing point. The cold, upper layers sink until the whole of the water has fallen in temperature to 4°C. , after which the colder layers, being lighter, will float on the surface and finally freeze. The ice becomes thicker by the freezing of the layer of water in contact with it, which falls below freezing point owing to the low temperature of the ice above.

Expansion of Gases.—The expansion of gases differs from that of solids and liquids not only in extent and in uniformity, but also in the fact that all gases, under proper conditions, expand by practically the same fraction for a given rise of temperature. The reason for this identity is to be found in the molecular similarity of gases.

Owing to the ease with which gases may be compressed, it is necessary to avoid fluctuations of pressure when measuring the coefficients of expansion. It is possible entirely to prevent the expansion of a gas on heating by applying moderate pressures, which is not the case with solids or liquids.

The coefficient of expansion of a gas at constant pressure may be determined by means of the apparatus illustrated in Fig. 14, which is a simplified form of Regnault's apparatus designed by the author for laboratory use. It consists of a bulb, B, of about 25 cubic centimetres capacity, placed at the end of one limb of a U-tube, the other end being open. The limb to which the bulb is attached is graduated so as to enable readings of the volume of the bulb and tube to be accurately taken. At the bend of the U-tube a T-piece, furnished with a tap, is sealed on, and the whole arrangement surrounded by a water-bath, the tube containing the tap being passed

through the cork. The temperature of the bath may be raised by means of a steam-coil, the ends of which also pass through the cork. In performing the experiment, mercury or strong sulphuric acid is made to occupy the bend of the U-tube to a point on the scale near the bulb, the gas being confined above the liquid. The columns of

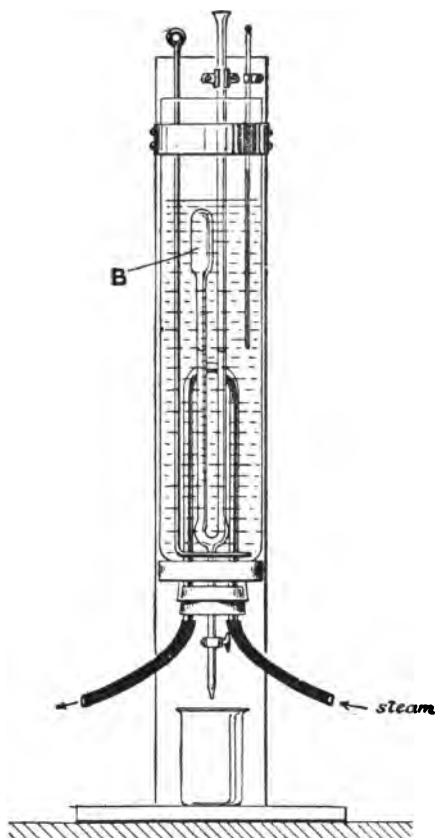


FIG. 14.—APPARATUS FOR DETERMINING THE COEFFICIENT OF EXPANSION OF GASES AT CONSTANT PRESSURE.

liquid in the limbs are brought to the same level by means of the tap, when the pressure of the enclosed gas will be equal to that of the atmosphere. This must always be done before taking a reading, in order to ensure constant pressure. The volume is then read, and the temperature of the bath noted. Steam is now passed through

the coil, and the bath stirred; a second reading of volume and temperature being taken when both are steady. The result is then calculated as follows:—

Let V_0 = the volume the gas would occupy at 0°C . (This may, if required, be observed directly by filling the bath with ice at the commencement.)

V_1 = volume at temperature t_1

V_2 = volume at temperature t_2

α = coefficient of expansion.

Then

$$V_1 = V_0 + (V_0 \times \alpha \times t_1) = V_0 (1 + \alpha t_1),$$

and similarly,

$$V_2 = V_0 (1 + \alpha t_2).$$

Hence

$$\frac{V_1}{V_2} = \frac{V_0 (1 + \alpha t_1)}{V_0 (1 + \alpha t_2)} = \frac{1 + \alpha t_1}{1 + \alpha t_2}.$$

In the above equations it is presumed that the coefficient α is the same between 0° and t_1° as between 0° and t_2° . That this is actually the case may be proved by taking readings every 5° from 0° , when it will be found that the increase in volume at 10° is twice that at 5° , and so on. If a curve be plotted connecting volume with temperature, it will be found to be a straight line. All the increases in volume must be taken with respect to that occupied at 0° ; or, in general, the expansion = $V_t - V_0$, where V_t is the volume at t° and V_0 the volume at 0° .

From the general expression $\frac{V_1}{V_2} = \frac{1 + \alpha t_1}{1 + \alpha t_2}$, the value of α may be calculated, as all the other quantities are known. The value should be corrected by adding the cubical coefficient of glass.

Example.—In the above apparatus, using air, the volume at 10°C . was 26.4 cubic centimetres. At 80°C . the volume was 32.9 cubic centimetres.

Hence

$$\frac{26.4}{32.9} = \frac{(1 + 10 \alpha)}{(1 + 80 \alpha)},$$

from which

$$\alpha = .00364.$$

Adding the cubical coefficient for glass, viz. .000026,

$$\alpha = .00366.$$

The coefficient of expansion of gases at constant pressure may

also be obtained by heating a bulb and tube containing the gas to a known temperature, the tube being kept horizontal, and containing a pellet of mercury to indicate the increase in volume. The internal capacity of the bulb, relative to that of a given length of tube, must be known, and the calculation made as above.

The contraction of a gas below 0°C . shows the same uniformity as that observed when cooling from higher temperatures to 0° . The value of the coefficient for gases is $\cdot 00366$, or $\frac{1}{273}$, and the expansion of gases may therefore be generalised in the form of a law, known as Charles's Law, which states that at constant pressure all gases expand by $\frac{1}{273}$ of their volume at 0°C . for a rise in temperature of 1°C . That is, if a gas occupied 273 cubic centimetres at 0°C ., its volume would become 274 c.c. at 1° ; 283 c.c. at 10° ; and so on, increasing by 1 c.c. per degree. It should be particularly noted that the increase is expressed as a fraction of the volume at 0°C ., and not a fraction of the volume at any other temperature.

If the value of the coefficient of expansion held indefinitely on lowering the temperature, the volume of a gas would finally become nil. Thus 273 c.c. at 0°C . become 263 at -10° ; 173 at -100° ; and at -273°C . should become 0. This cannot be imagined, and with every gas physical changes would occur which would cause an alteration in properties, so that the law would no longer hold. The conception of a perfect gas, however, which would continuously obey Charles's law, is useful as a standard of reference. The temperature of -273°C ., at which a perfect gas would possess zero volume, is called the absolute zero of temperature. It may be added here that different gases do not possess exactly the same coefficient of expansion, although for gases well above the temperature at which they liquefy the variation from the figure $\frac{1}{273}$ is very small. When a gas is near its temperature of liquefaction, the divergence from Charles's law is quite appreciable.

The expansion of gases, and problems arising therefrom, will be further referred to in the chapter dealing with the general properties of gases.

CHAPTER V.

PRACTICAL APPLICATIONS OF THE PROPERTY OF EXPANSION.

IN all cases where bodies are subjected to alterations of temperature, expansion and contraction must be constantly taking place. Although in many instances this effect may be ignored, it is of the highest importance in other cases to make due allowance for free expansion, or to take such steps as will reduce the effect of the expansion to a minimum. In addition, a number of useful mechanisms depend for their action on the expansion of one or more of the parts of which they are composed. It is proposed to deal with a number of the various applications of this property in the present chapter; leaving, however, the utilisation of expansion for the purpose of measuring temperature to a subsequent chapter.

Expansion of Rails.—A line of railway, with the rails bolted together, forms a practically continuous bar of metal, and is subject to all the fluctuations of atmospheric temperature. Unless due allowance were made, the rails on a hot day would tend to arch upwards, and in doing so would disturb the sleepers on which they are laid and thus make the line uneven. This is prevented by the use of slotted or elongated bolt-holes in the rails themselves, and in the fish-plates joining two consecutive rails. When bolted together, a small space is left between the ends of the rails, which may therefore expand freely over the bolts. The space to be allowed between the ends may be calculated in the manner indicated in the following example.

Example.—If steel rails, 20 feet long, are laid at a temperature of 10°C. , allowance should be made sufficient to take the increased length at 55°C. , which may be attained on a hot day in summer. As the coefficient of expansion of steel is $\cdot 000011$ per $^{\circ}\text{C.}$, the length at 55° would be

$$20 + (\cdot 000011 \times 20 \times 45) \text{ feet} = 20\cdot 01 \text{ feet (nearly).}$$

The space allowance must therefore be $\cdot 01$ of a foot, or nearly $\frac{1}{8}$ of an inch.

As the rails expand freely in both directions, the movement at either end is equal to one-half of the total expansion. Hence the space will be filled by two consecutive rails expanding through half the interval allowed, the same occurring at the other end of each rail.

Some engineers have questioned the utility of making an expansion space, and it is possible that the results ensuing from the absence of the space have been exaggerated. It is customary, in some cases, to lay tram-lines without spaces, and even to weld the ends together in position by means of thermit; and it is claimed that no serious consequences ensue. In any case, the space should be left as small as possible, in order to reduce the jolting of the vehicle at the joints to a minimum.

Expansion of Boilers.—The difficulty to be contended with in boilers is the unequal expansion of the different portions, owing to one part being at a higher temperature than another. The tendency is to cause buckling, owing to the expansive force, leaving the boiler distorted and weakened. This tendency is manifested at the ends, which are pushed outwards by the longitudinal expansion, and owing to difference of temperature in different parts, a greater expansive force is exerted on some sections of the end than on others, producing local strains. Permanent distortion may largely be prevented by the use of tie-rods, which pass through the length of the boiler and are fastened at each end. These serve largely to distribute the strain, and, on contracting, tend to pull the expanded portion back to its original position.

Another effect of unequal expansion is the tendency to shear the rivets in the region of the parts which expand most. Wherever possible, such parts should be strengthened by tie-rods or other means. In the flue of a stationary boiler the temperature on the surface in contact with the fire is much greater than that possessed by the other surface, which is at the temperature of the water in the boiler. The result is a tendency to arch outwards, as the outer surface expands more than the inner, the effect being to weaken the riveted joints. The flues are strengthened by the presence of cross-tubes, riveted to the flue at both ends, and which also serve as heating surfaces and to promote circulation.

Reference may be made here to the statement, common in text-books, that boiler-plates are fastened together with hot rivets because the plates are drawn close together by the contraction of the hot rivet. The real reason why hot rivets are used is that it would be a practical impossibility to form the head if the rivet were cold. Although the rivet, if rapidly finished off, may tend by its longitudinal

contraction to draw the plates together, a lateral contraction occurs also, with the result that a space is formed between the rivet and the hole, and leakages of steam frequently occur on this account. To avoid this the leaky rivet is caulked to ensure a good contact of the rivet head with the plate, and thus close all channels through which steam might escape.

Steam-pipe Joints.—Owing to the expansion of pipes conveying steam, there is a tendency for the joints to break and cause a leakage of the steam. This is avoided by making telescopic joints, so that, on expansion, the pipes may slide over each other, tightness being secured by a stuffing gland. The difficulty may also be overcome by inserting elbows or loops in the length of the pipes, which possess sufficient flexibility to take up the expansion. A third method is to join the ends of two consecutive pipes to a flexible copper chamber, which gives to the expansion.

Expansion of Pistons.—In steam-engines, and also in internal combustion engines, the temperature of the piston is higher than the average temperature of the cylinder, and hence will expand more. A tight joint is secured by the use of piston rings, which spring outwards and make contact with the cylinder. The expansion is taken up by the piston ring, the ends of which are left a small distance apart to allow for the extension, and thus prevent the piston from jamming.

In some forms of petrol engines, used for automobiles, the piston ring is continuous, and made of such a size as exactly to fit the cylinder when the engine is working; the piston and ring having increased in diameter. This method prevents leakage through the piston, which is always liable to occur through the space between the ends of the piston ring when not continuous. On the other hand, much more exact fitting is required to ensure a good contact between the ring and cylinder.

Shrinking of Tyres and Angle-iron Rings.—The iron tires of wheels are made to fit tightly on the wooden rim by placing them in position whilst red-hot. The contraction on cooling ensures a tight grip on the rim. The diminution in diameter may be calculated as follows:—

Example.—An iron ring having a mean diameter of 2 feet at 850° C., will, on cooling to 10° C., possess a mean diameter of

$$24 - (24 \times .000014 \times 840 \text{ inches}) = 23.718 \text{ inches.}$$

Hence the diameter contracts by .282 of an inch, or more than $\frac{1}{4}$ of an inch.

It should be noted in the calculation that the ring shrinks to the

same extent as would a hot iron rod or spoke placed across it; for since the ring diminishes in circumference by $(\pi d \times a \times t)$, where t is the fall in temperature, the diameter will be lessened by

$$\frac{\pi d \times a \times t}{\pi} = d \times a \times t.$$

The mean coefficient of expansion of iron (linear) between 10° and 850° C.—a full cherry-red heat—is $\cdot 000014$.

It will be seen from the foregoing example that the increase in size of an iron ring, when heated to a full cherry-red, is rather more than $\frac{1}{8}$ of an inch per foot of diameter. This permits of the ring being easily slipped over a rim which has a diameter equal to, or slightly more than that of the ring when cold.

Angle-iron rings are placed on the ends of the barrels of boilers, etc., in the same way. The ring must be placed exactly in its correct position before cooling, as afterwards it would be difficult to move. Strengthening bands round cylinders of various kinds are often shrunk into position in a like manner. The sections of a gun are similarly shrunk together.

Permanent Decrease in Size by Rapid Cooling.—A bar of wrought iron, if heated to a full red heat and suddenly quenched in cold water, undergoes a permanent decrease in length; and if again heated and quenched will undergo a further contraction. Box found that a bar of iron 40 inches long, and $\frac{7}{8}$ of an inch diameter, contracted by $\frac{1}{1000}$ part of its length on the first quenching, and continued to contract by diminishing amounts up to 20 quenchings, at the end of which the total contraction was $\frac{1}{100}$ part of the original length, or $\cdot 4$ of an inch. This property is sometimes utilised in reducing the size of a hole in wrought iron which has accidentally been bored too large. Experiments were also made by Box on the permanent contraction of a tire originally 7 feet in diameter, with the result that after 11 heatings and quenchings the diameter was diminished by $1\frac{1}{4}$ inch.

Contraction of Metal Castings on Cooling.—The size of a casting when cold is, in general, less than that possessed when in the liquid state. In most cases, the contraction takes place in two stages, viz. a contraction during solidification, and a further shrinkage of the hot solid. Cast iron, bismuth, and antimony, possess the exceptional property of expanding in the act of solidification; and in the case of bismuth this expansion is so great as to exceed the subsequent contraction of the hot solid. Hence cold bismuth possesses a greater volume than the liquid metal. In the case of cast iron, the con-

traction on cooling is greater than the expansion on solidification ; hence the cold casting is smaller than the mould in which the molten metal is poured. With brass, lead, tin, zinc, aluminium, and other metals and alloys, a shrinkage occurs both on setting and in the subsequent cooling. The relation between the volumes when cold and molten respectively is of importance in the making of patterns. By making due allowance for the volume changes, the size of the pattern may be regulated so as to produce a casting of a given size when cold.

The following table gives the results of Roberts-Austen's experiments on the relation between the cold and molten volumes of different metals :—

Name	Percentage of Increase or Decrease in Volume on Changing from Cold Solid to Liquid
Copper	Increase of 7·1
Lead	„ 9·93
Tin	„ 6·76
Zinc	„ 11·1
Silver	„ 11·2
Iron (Cleveland Foundry) . .	„ 1·02
Bismuth	Decrease of 2·3

In considering a casting of any given shape, it is correct to assume that the shrinkage along any side is proportional to its length. Thus in casting a rectangular block, 1 foot by 6 inches by 3 inches, the contraction in each direction would be as 12 : 6 : 3. Hence if the contraction per foot be known, the pattern may be made proportionately longer in each direction. The contraction per foot of length for several metals and alloys is appended :—

Name	Contraction per foot of Pattern or Mould
Cast iron . . .	$\frac{1}{10}$ of an inch
Brass	$\frac{1}{8}$ to $\frac{3}{16}$ of an inch
Gun metal . . .	$\frac{1}{5}$ to $\frac{3}{16}$ „
Zinc	$\frac{1}{2}$ of an inch
Aluminium . . .	$\frac{1}{2}$ „

The above figures represent the allowance made in practice for the metals enumerated, and are only approximate, as the total contraction depends on the temperature at which the metal is poured, and the expansion of the mould. The addition of the value to each foot of length ensures a close approximation to the desired size in the cold casting; and the pattern is therefore made by adding to each finished dimension the amount indicated in the table. Thus the size of a pattern for a gun-metal casting, of finished dimensions 2 feet \times 1 foot \times 6 inches, will be 2 feet $\frac{3}{8}$ inch \times 1 foot $\frac{3}{8}$ inch \times 6 $\frac{3}{4}$ inches. To save the labour involved in calculating the allowance to be made for a given dimension, special rules are made, on which the markings are longer than those of a standard rule by the proportionate amount of contraction of the metal. For gun metal, a 2 feet contraction rule is in reality 24 $\frac{3}{8}$ inches long, and is divided into 24 equal parts, these being sub-divided into quarters, eighths, and sixteenths. Contraction rules to suit various metals and alloys are in use for the purposes of pattern making, and ensure correct size in the finished casting.

Allowance for Expansion in Girders.—If long iron or steel girders, as used for bridges, roofs, etc., were rigidly fastened to their masonry supports, the effect of expansion would be either to distort the shape of the girder, or break down the supports. In the case of large steel bridges, the difference between the minimum and maximum length is considerable, and free allowance for expansion is absolutely necessary.

Example.—The total length of the Forth Bridge is 8100 feet. Taking the difference between the lowest winter temperature and the hottest summer temperature as 45° C., the difference in length between the two extremes is $(8100 \times .0000117 \times 45)$ feet = 4.265 feet.

The expansion is taken up by allowing the ends of the girders free movement over rollers, upon which they are mounted; or by attaching the free end of the girder to a knuckle which permits of sufficient movement in either direction. A third method is to insert lattice-work with free joints in the girder, which is capable of movement outwards or inwards. The steel rails laid over a bridge of the same material will, of course, expand or contract by the same amount as the bridge itself.

The distortion due to expansion is strikingly shown when a fire occurs in a building constructed with a steel framework. The walls of the building are pushed outward, and the girders themselves become twisted and bent out of shape.

Breakage Due to Sudden Expansion or Contraction.—A tumbler, or other thick glass vessel, when suddenly heated by pouring in hot

water, is liable to break or crack. This arises from the fact that glass is a bad conductor of heat, and is brittle; hence when heated suddenly the superficial layer expands before the heat has penetrated to the rest of the material. A strain sufficient to crack the glass is thus produced; and for a like reason the sudden contraction of the surface produced by the rapid cooling of hot glass in water causes breakage. Molten glass, however, may be dropped into water without breaking, as the molten interior gives way to the contraction of the outer layer. Glass thus treated, however, is peculiarly unstable, and will break into fragments on penetrating the outer layer. The well-known Rupert's drops and Bologna phials are examples of glass which has been quenched in this manner.

Thin glass vessels are not so liable to break as thick ones on sudden heating or cooling, owing to the short time required for the outer and inner layers to attain the same temperature, and to the possession of greater flexibility. Hence beakers and flasks intended for boiling liquids are made as thin as possible, consistent with strength. Some kinds of glass are specially flexible, and may be safely heated or cooled suddenly over a larger range of temperature than ordinary glass. Jena glass is superior to others in this respect, although other special "resistance" glasses are nearly as good.

Quartz vessels, which may now be obtained, show a remarkable resistance to breakage on sudden heating or cooling, and may be plunged at a red heat into water without damage. This property is probably due to the very low coefficient of expansion of the material, combined with a high degree of flexibility. It may be added that metal vessels will endure a sudden expansion or contraction safely owing to the rapid attainment of the same temperature throughout, and to the possession of the properties of malleability and ductility, owing to which metals readily alter in shape.

Correction of Measures of Length.—The standards of length in different countries are usually bars of bronze on which fine marks are engraved at certain distances. The British standard yard is the distance between two fine lines drawn on pieces of platinum inserted in a bronze bar. It is obviously necessary to specify a temperature at which the true yard is defined, and $62^{\circ}\text{ F.} = 16^{\circ}\text{ C.}$, has been selected as the standard temperature. The advantage gained by defining the yard with respect to this temperature is that the average temperature of a room in Britain is approximately 62° F. , and fairly exact comparisons may be made without special temperature precautions. The standard metre is defined with respect to the tem-

perature of melting ice, or 0°C. , which is a definite temperature easily obtained experimentally.

Many accurate copies of the true standards are in existence, from which the various workshop gauges are made. It is necessary, when making accurate measurements of length—as in establishing a base line for an accurate survey—to make due allowance for the alteration in length of the measuring arrangements caused by expansion or contraction. This may be accomplished by calculation from the known coefficient of expansion of the material, or by using a standard of length which is so constructed as to be of constant length at all atmospheric temperatures. The principle upon which such standards are made will now be described.

Measures of Constant Length.—The fact that metals on heating expand by different amounts has been applied to constructing a measure of constant length, the principle of which will be understood from Fig. 15. The constant length is the space between two lines

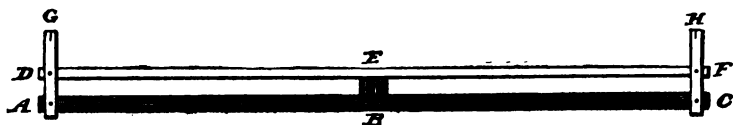


FIG. 15.—PRINCIPLE OF MEASURE OF CONSTANT LENGTH.

engraved on the ends G and H of the bars G D A, H F C, which are fastened at the lower end to a rod of brass, A B C. At the points D and F, distant by $\frac{1}{3}$ of the length of A G or H C, is fastened a bar of iron D F. As the coefficient of expansion of iron is to that of brass nearly as 3 : 5 (exactly, as 13 : 21), it follows that a rise of temperature will cause the extremities G and H to be moved as much outwards by the iron bar as the brass bar tends to pull them inwards, the net result being that the distance between G and H is constant. On cooling, the contraction of the brass bar tends to move G and H outwards, but this is again neutralised by the contraction of the iron bar. Constancy of length is therefore secured when the cross-bars are distant from the ends G and H in the ratio of the respective coefficients of expansion. Zinc is sometimes used instead of brass, in which case the ratio $\frac{H C}{H F} = \frac{.0000292}{.0000117} = \frac{2.5}{1}$. Instruments based on this principle are of great service in the accurate measurement of base lines for surveys, as the necessity of taking temperature readings, and thereby correcting for expansion, is avoided.

It is highly probable that for all but the most exact work, nickel-

steel measures will supersede other forms. The extremely low coefficient of expansion of this alloy has previously been referred to.

Correction of Measures of Volume.—Measures of volume, like measures of length, are subject to fluctuations owing to alterations of temperature. The British standards of volume are constructed of brass, and defined with respect to 62° F. A standard litre, or 1000 cubic centimetres, should hold exactly 1000 grams of water at 4° C. When standardised to read correct volume at another temperature—such as 15° C.—a litre measure should possess the same volume at 15° C. as that occupied by 1000 grams of water at 4° C. It is more convenient, in practice, to use a vessel of standard size when at an average temperature, e.g. 15° C., than one standardised at 4° C., as in all ordinary measurements the discrepancy caused by expansion or contraction may be neglected.

Example.—A litre flask, correct at 15° C., would increase in volume at 20° C. by $(1 \times .000026 \times 5) = .00013$ litre, or .13 of a cubic centimetre; and at 10° C. would diminish in volume by a like amount. The variations of temperature in a room in which the vessel would be used would not greatly exceed 5° C. on either side of 15° C., and the alteration in volume is for ordinary purposes negligible. If made correct at 4° C., the error at 20° C. would be .416 of a cubic centimetre, or more than 3 times as great as before.

The glass measures usually sold, such as flasks, pipettes, burettes, and measuring cylinders, are only approximately correct, and, wherever great accuracy is required, should be tested at the National Physical Laboratory, and a table of corrections obtained. The same applies to the metal vessels used for the measurement of volume commercially in Britain. When the exact volume at a given temperature is known, the capacity at any other temperature may be calculated from the coefficient of expansion.

Correction for Expansion of Liquids.—The comparatively high coefficient of expansion of liquids causes a considerable alteration in volume for a moderate rise of temperature. When liquids such as petroleum and its extracts, or alcohol, are purchased in bulk, an appreciable error might arise unless the temperature be taken into account. Thus 100 gallons of alcohol at 10° C. expand to 101.1 gallons at 20° C., or more than 1 per cent. for a rise of 10° C. The increase in the case of petroleum is slightly larger; and hence it is necessary, in order to secure the correct quantity, to allow a greater volume according to the temperature. This can be accomplished readily by specifying a definite weight to represent 1 gallon, and calculating the extra volume from the observed specific gravity.

Example.—1 gallon of a liquid, of specific gravity = $\cdot 80$ at 62° F., would weigh 8 lb. If the coefficient of expansion = $\cdot 001$ per 1° C., then at 80° F. the volume would increase by 1 per cent., and the specific gravity would fall to $\cdot 792$. If the gallon of 8 lb. were specified as the standard, it would be necessary to provide an increased volume at 80° F. in the ratio of $\frac{\cdot 800}{\cdot 792}$, or an extra gallon for every hundred. Or, in general, $\frac{\cdot 80}{\text{observed sp. gr.}} = \text{volume in gallons which weigh 8 lb.}$

The specific gravity of a liquid frequently furnishes a clue as to its purity, as in the cases of milk, spirits, oils, etc. In other instances—e.g. acids and alkaline solutions—the specific gravity is an indication of the chemical strength. In all these cases temperature precautions are necessary. The specific gravity at any temperature is the ratio of the weight of 1 cubic centimetre of the substance compared with that of 1 cubic centimetre of water at 4° C. It would be very inconvenient in practice to reduce the temperature of a liquid to 4° C. to obtain the weight of 1 c.c., and hence it is customary to determine the figure for the liquid at the more convenient temperature of 15° C. If 1 c.c. of a liquid at 15° C. weighs 1.45 grams, its specific gravity at 15° C. is 1.45, as 1 c.c. of water at 4° C. weighs 1 gram. It should be noted that if both liquid and water are weighed at 15° C. a slightly different result is obtained, as 1 c.c. of water at 15° C. weighs $\cdot 999$ gram. In recording a result, it is customary to insert the temperatures; thus “specific gravity = $1.45 \left(\frac{15^{\circ}}{15^{\circ}} \right)$ ” means that the substance at 15° C. is 1.45 times as heavy as an equal bulk of water at 15° C. The true specific gravity at t° would be expressed thus: “Specific gravity = $\left(\frac{t^{\circ}}{4} \right)$,” signifying that the weight of 1 c.c. at t° had been compared with that of 1 c.c. of water at 4° C. Much confusion may arise unless this method of recording the result is observed.

Another instance in which an appreciable error may arise owing to the expansion of liquids is found in the use of standard solutions for chemical analysis. This source of error is too frequently ignored, and volumes of the solution are often recorded to $\frac{1}{100}$ of a cubic centimetre when the expansion error may be as much as $\frac{1}{10}$ of a c.c. When a standard solution is made up, the temperature should be noted, and in using afterwards the temperature should not vary by more than 5° C. on either side of the standard temperature. In

"normal" solutions, a difference of 5°C. alters the volume by $\cdot 2$ of a c.c. per 100, or $\cdot 2$ per cent.—a quite appreciable error in exact analysis. An example will make this clear.

Example.—Normal sulphuric acid (49 grams per litre, or nearly 5 per cent. acid), has a mean coefficient of expansion, between 15°C. and 25°C. , of $\cdot 0004$. If correct at 15°C. , and used (on a hot day) at 25°C. , the increase in volume per 100 c.c. would be $(100 \times \cdot 0004 \times 10) = \cdot 4$ c.c. If only 25 c.c. were used in the determination, the error would still be $\cdot 1$ of a c.c., an amount which is often of importance. It is therefore evident that refinements in reading the volume are useless unless the temperature be allowed for.

Thermo-Regulators.—The property of expansion is utilised in the instruments known as thermo-regulators, the object of which is to secure a constant temperature automatically. A simple form is illustrated in Fig. 16, intended for use in conjunction with a gas supply, which is regulated so as to maintain a constant temperature in a hot-air oven. It consists of a large bulb of mercury connected to a tube of fine bore T, widened at the upper end so as to receive the gas inlet G, which is inserted so as nearly to touch the top of the mercury column. The gas escapes through the side-tube S, which is connected to a burner beneath the oven. On placing the bulb in the oven, the mercury will expand until the opening of the inlet-tube G is covered, and the gas supply cut off. The temperature then falls, and the mercury contracts, again admitting gas to the burner, which is never entirely extinguished owing to the small constant supply of gas which passes through a fine hole H, in the inlet-tube. The temperature at which the main supply is cut off may be regulated by the screw D, which enables the column of mercury in T to be brought to any desired distance from the end of the gas inlet-tube. The adjustment may be carried out so as to maintain a temperature in the oven not varying by more than 1 or 2 degrees from that required.

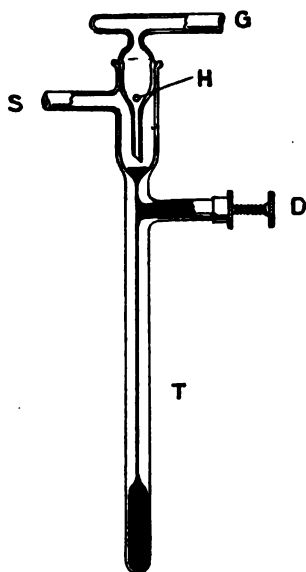


FIG. 16.
THERMO-REGULATOR.

More sensitive thermo-regulators may be made by using a liquid of high coefficient of expansion to push up the mercury column. Thus alcohol, for a given rise of temperature, expands 6 times as much as mercury, and is therefore more sensitive when used in a thermostat. It cannot be used above 79°C. , at which it boils; but for higher temperatures, up to about 140°C. , turpentine may be used. A very close approach to a constant temperature can be obtained with these liquids. In some forms air is employed, which by expanding raises the mercury column.

Many forms of thermo-regulator are in use, of which mention may be made of a specially sensitive type used in the electrical testing department of the National Physical Laboratory. In this case the compound formed by absorbing ammonia gas in silver chloride is used in a tube connected to a mercury column, which, on rising, closes the gas inlet. This compound possesses a high vapour pressure, which increases considerably for a small rise of temperature, and hence causes the mercury column to close the inlet, either wholly or in part, whenever a very slight increase of temperature occurs. This arrangement forms a very sensitive thermo-regulator.

Fire Alarms.—Many devices are in use for raising an alarm when the temperature of a room rises to such an extent as to indicate the existence of a fire. One form of fire-alarm consists of a mercury thermometer made with a large bulb and wide-bore tube. Into the bulb is sealed a platinum wire, to which is connected one terminal of an electric bell. Another piece of platinum wire passes through the open end of the tube, and may be raised or lowered so that its end is opposite any temperature on the scale. This wire is connected with the other terminal of the bell, and when the mercury rises so as to touch its extremity, the circuit is completed and the bell rings. In an ordinary room, on a hot summer day, the temperature seldom rises above $80^{\circ}\text{F.} = 26.5^{\circ}\text{C.}$, and hence if the instrument were adjusted to ring at 100°F. , and the bell rang, a fire in the room itself or the vicinity would be indicated. In stores for inflammable liquids, etc., the instrument would be set to ring at a lower temperature, and thus would indicate the existence of dangerous conditions.

In another form of fire-alarm a flexible metallic drum, filled with air, is used. When the air inside the drum is heated, the expansion causes the flexible end of the drum to make contact with a metallic stop, and thus to complete an electric bell circuit. The distance of the stop from the end of the drum may be regulated by a screw, and hence the temperature at which the bell rings may be regulated.

The advantage of this form is its portability, and the absence of any glass parts liable to breakage. Many serious fires have undoubtedly been prevented by the use of fire-alarms, owing to the early warning obtained.

Principle of the Compound Strip.—If two pieces of different metals be fastened together, either by soldering or riveting, the compound piece thus formed will, in general, undergo a change in shape on heating or cooling. If, for example, a strip of brass is fastened to one of iron, the effect of heating will be to make the compound strip assume a curved shape, the brass part occupying the outer portion of the curve. Cooling will also cause arching, but in this case the brass will occupy the inner portion of the curve. The alteration in shape is due to the different amounts by which brass and iron expand on heating, or contract on cooling; hence if each component has the same length at ordinary temperatures, the brass, which possesses the greater coefficient of expansion, will be longer than the iron on heating, and shorter on cooling. The outer portion of the curve is longer than the inner portion, and hence will always be occupied by the metal which, under the circumstances, is the longer. This alteration in shape has been utilised in the construction of numerous instruments, some of which will be described in the succeeding paragraphs.

Compensated Balance Wheel for Watches.—The principle of this wheel may be understood by reference to Fig. 17, A. The rim is a

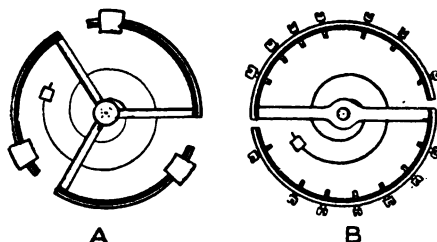


FIG. 17.—COMPENSATED BALANCE-WHEEL OF WATCH.

compound strip of brass and steel, the brass being on the outer side. In the form illustrated the rim is made in three segments, each of which is attached at one end to a spoke, the other end being free. Each segment is provided with an adjustable weight, and the object is to arrange that the centre of gravity of the rim and weights shall remain at a constant distance from the pivot at all temperatures, in which case the period of oscillation will be uniform. The effect of

a rise in temperature is to cause the spokes to increase in length, thereby tending to move the centre of gravity of the rim and weights further from the pivot, in which case the period of oscillation would be slower. Simultaneously, however, the rim increases its curvature, or forms a more acute arch, thus causing the weights to move nearer the pivot, and consequently bringing the centre of gravity inwards. If these opposite tendencies be exactly equal, the result is to obtain a constant distance between the centre of gravity and the pivot, and this result may be attained by adjusting the position of the weights on the segments, as it is evident that the displacement of the centre of gravity is greatest when the weights are at the free end, and diminishes as the weights are moved along the segment. The correct position is found by trial of the watch at different temperatures.

Fig. 17, B, represents a common form of compensated balance wheel. The centre of gravity of the rim may be altered in position by screwing the studs outwards or inwards, and the adjustment is finer than that obtained by the use of sliding weights. The rim consists of two segments, each attached at one end to a single bar or spoke. The correct adjustment for temperature is a tedious process, involving frequent alterations and trials at different temperatures. Many cheap watches are provided with a wheel of this type for the sake of appearance, but have never undergone a correct adjustment. It is quite possible for such a watch to keep worse time than one furnished with an ordinary wheel, as the centre of gravity may undergo a greater displacement than that produced by expansion in a simple wheel.

The Pearson Fire-Alarm.—In this device the increased arching of a compound strip is made to complete an electric circuit and thus cause a bell to ring. A thin, bi-metallic strip, about 6 inches in length, is made into the form of an arch and fastened at both ends. One wire of the bell circuit is connected to the compound strip, and the other to a screw, the point of which may be brought to any desired distance from the centre of the arched strip. When the temperature rises, the strip forms a more acute arch, and touches the screw, thus completing the circuit and giving the alarm. The arrangement permits of adjustment for any desired temperature, by altering the distance of the point of the screw from the strip. By employing very thin metals for the compound strip, the sensitiveness of the instrument is greatly increased, as the temperature of the surrounding air is then rapidly attained. By placing an instrument in each room of a building, and connecting indicators in the circuits, it is possible to locate the room in which a dangerous temperature

exists, as the fire-alarm bears the same relation to the electric circuit as an ordinary push. This form of fire-alarm is much used, being more sensitive, and less liable to breakage, than other forms in which an expanding liquid is used. Compound strip fire-alarms are much used in cold stores, to give warning of either too high or too low temperatures, and are called in this connection "thermostats."

Breguet's Metallic Thermometer.—This instrument consists of a thin, triple strip of platinum, gold, and silver, the gold strip being in the centre. The strip is made into a spiral, with the silver face innermost; one end of the spiral being fixed, and the other end, to which a light pointer is attached, being free to move. When the temperature rises, the silver expands more than the gold or platinum, causing the spiral to unwind, the reverse effect being produced on cooling. The pointer at the free end of the spiral moves over a scale, graduated in degrees by comparison with an ordinary thermometer. The arrangement is very sensitive, but has little practical utility.

Steam-Traps, or Water Ejectors.—In steam pipes and the cylinders of steam-engines, condensation takes place owing to cooling, and various devices are in use for removing the condensed water automatically. These mechanisms are known as steam-traps, and work on the common principle of causing an outlet to open when cooling occurs, through which the water is ejected by steam pressure; the outlet closing when the temperature rises. Typical examples will now be described.

Vaughan and Stubbs' steam-trap (Fig. 18) consists of a brass tube B, which communicates with the steam-pipe P, and is surrounded by an iron tube A. The lower end of the brass tube is made conical so as to fit on the valve V, and is open to the outlet O, when not in contact with V. When the tube B is full of steam, its length is such as to cause it to press firmly on V, and consequently no steam escapes. When, however, a quantity of condensed water has en-

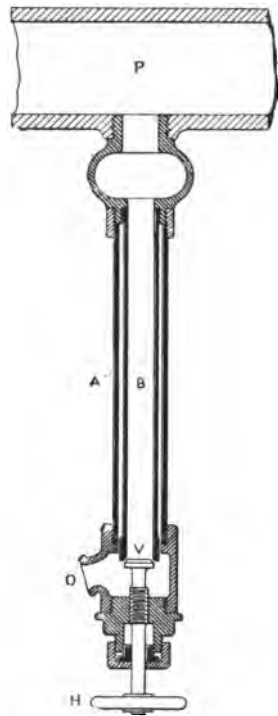


FIG. 18.—VAUGHAN AND STUBBS' STEAM-TRAP.

tered B from the steam-pipe, the temperature falls, and consequently the tube contracts in length and breaks the joint made with V. The condensed water is then driven by the steam pressure through the outlet, after which the opening again closes owing to the expansion of B occasioned by the rise of temperature. The valve V may be adjusted for any pressure of steam by means of the handle H, so that when the tube is full of steam the outlet is closed. At high pressures the valve V is lower than in the case of lesser pressures, as the temperature is higher, and consequently the expansion of the tube greater. Incidentally, the tube A participates to some extent in the alterations of length, but owing to contact with the atmosphere the changes are small; and, in addition, the tube B, being made of brass, expands more than A, which is made of iron, for a given rise of temperature. The drawback of the arrangement is that the tube B, if overheated, will press so hard on the valve V as to cause the tube to distort, and thus make an imperfect junction with V.

A more modern form of steam-trap, known as the "Midget," is illustrated in Fig. 19, and depends for its action on the varying ex-

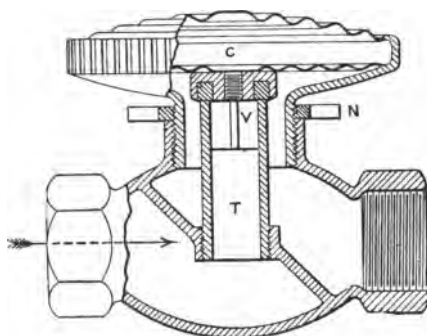


FIG. 19.—"MIDGET" STEAM-TRAP.

pansive force exerted by a saturated vapour at different temperatures. The valve V is held on its seat by the lower part of a corrugated chamber C, which contains a highly volatile liquid, such as light petroleum spirit, and is hermetically sealed. The pressure of a saturated vapour (*i.e.* one in contact with its own liquid) varies considerably with the temperature, particularly when the liquid is above its normal boiling point; the variations greatly exceeding those experienced by a gas under the same conditions. Hence a

small alteration of temperature will make a considerable difference in the force with which the valve V is held on its seat. The lower diaphragm of the chamber C must be adjusted so that the pressure exerted on V is just greater than the steam pressure when the valve is full of steam. This adjustment is made by raising or lowering the chamber C, a lock-nut N serving to hold it fast in any given position. When no water is present, the steam, which enters from the steam-pipe in the direction of the arrow, bathes the under side of the corrugated chamber, and the valve V is prevented from lifting by the elastic force of the contained vapour. When water accumulates in the trap, the temperature falls, causing a considerable reduction of the pressure of the vapour in C; consequently the valve is lifted and the water ejected by the steam pressure. After the removal of the water the temperature will again rise, and the valve close. This steam-trap is extremely sensitive, and is capable of ejecting a teaspoonful of water without any escape of steam. The "Imp" steam-trap is an improved form of the "Midget."

A third form of steam-trap, suitable for high pressures, is shown in Fig. 20, which represents a recent production of Holden and

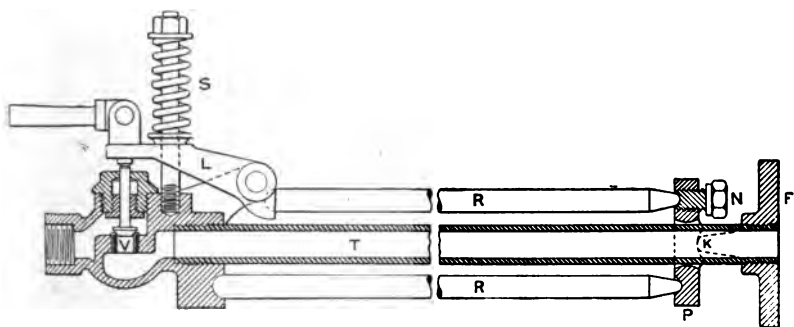


FIG. 20.—HOLDEN AND BROOKF'S STEAM-TRAP.

Brooke, of Manchester. In this, as in the "Midget" trap, the joint with the outlet is not made directly with the expanding tube. Instead of this, a valve V, held in position by a spring S, operating on the bell-crank lever L, closes the outlet. Two rods R R run parallel with the tube T, the right-hand end of these rods bearing against the piece P, which is independent of the tube, and capable of rocking on the knife-edge K, which is a prolongation of the piece F. Assuming the trap to be cold, and the valve pressed on its seat, the adjustment is made by turning the stud N, thereby pressing the upper

rod against the bell-crank lever, and causing the valve to lift against the pressure of the spring. The motion of the rod is magnified about five times by the lever ; and the adjustment must be such as to cause the outlet to open when water accumulates, but to close when the trap is full of steam. The closing of the valve is effected indirectly by the expansion of the tube, which carries the lever attached to it away from the rods, and permits the spring to close the valve. When a quantity of water settles in the tube T, and the temperature falls in consequence, the tube contracts, and presses the lever on the upper rod, thereby causing the spring to lift and the valve to open. The arrangements of the two rods R R, and the rocking-piece P, obviate any bending strain in the tube T. This steam-trap will open when the temperature falls by 5 per cent., and can be used directly on a cylinder or steam-pipe.

Of the numerous other forms of steam-traps, mention may be made of those in which the principle of the compound strip is employed. In these the arching of a semicircular compound strip of two metals is utilised to lift the valve, whilst the straightening of the strip causes it to close the outlet. Such steam-traps suffer from the defect that overheating will produce distortion, and cause the valve to make a defective joint with its seat.

Compensated Pendulums.—The period of vibration of a pendulum varies directly as the square root of the length, and consequently a pendulum subjected to changes of temperature will show a variation in the time of vibration, as the length alters with the temperature. Any mechanism, such as a clock, controlled by a pendulum, will therefore be subject to alterations in the time of movement ; thus in warm weather, when the pendulum is longer, a clock will lose time, and conversely will gain time in cold weather. The object of compensated pendulums is to maintain the effective length—that is, the distance between the point of suspension and centre of oscillation—constant at all temperatures. This may be effected by utilising the different expansion of two substances in such a manner that the vertical motion of the centre of oscillation, due to one substance expanding or contracting, is exactly balanced by a movement in the opposite direction due to the other material.

Two simple forms of compensated pendulums are shown in Fig. 21, where A represents a wooden pendulum with a zinc bob, which fits loosely round the wood. The wooden rod, on expanding, tends to lower the centre of gravity and thus increase the effective length of the pendulum ; the zinc bob, however, expands simultaneously in an upward direction, thereby tending to raise the centre of gravity.

If the two opposing tendencies are equal, the period of oscillation will remain constant ; and as the zinc has a much higher coefficient of expansion than the wood, the smaller length of zinc may be made to compensate the expansion of the greater length of wood. In the same figure, B represents Graham's mercurial pendulum, which is similar in principle. The bob consists of a vessel containing mercury, the rod being made of iron or other metal. The quantity of mercury in the vessel is adjusted so that its expansion in an upward direction counteracts that of the rod downwards. When both rod and vessel

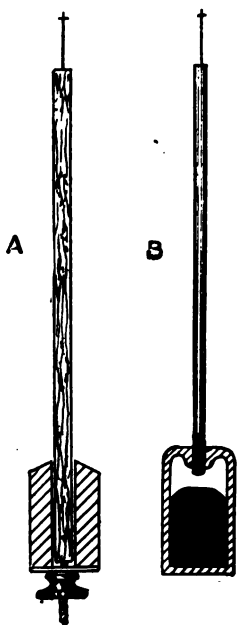


FIG. 21.—COMPENSATED PENDULUMS.



FIG. 22.—HARRISON'S GRIDIRON PENDULUM.

are made of iron, the height of the mercury should be about $\frac{1}{6}$ of the total length of the pendulum to secure compensation.

Harrison's gridiron pendulum consists of a heavy bob suspended from a framework composed of alternate rods of iron and brass, as shown in Fig. 22, where the black rods are of iron and the others of brass. These rods are able to move freely upwards or downwards between cross-pieces, and it will be observed that, whilst the expansion of the iron rods tends to lower the bob, the expansion of

the brass rods tends to raise it. If the total length of the iron rods is about $1\frac{2}{3}$ times that of the brass rods, these movements will counteract one another, as the coefficient of expansion of brass is about $1\frac{2}{3}$ times as great as that of iron. Considered from the standpoint of the expansion produced, the symmetrical rods of iron and brass respectively may be regarded as a single rod; and consequently compensation will be secured when the two iron rods on either side of the centre, together with the rod carrying the bob, have a combined length of $1\frac{2}{3}$ times—or more accurately $1\frac{8}{13}$ times—that of the joint length of the two brass rods on either side. The object in duplicating the rods is to secure an evenly balanced pendulum.

The use of the non-expansive nickel-steel alloy would largely obviate the necessity for compensated pendulums, and it is highly probable that this alloy will be largely employed for this and other purposes in the future.

CHAPTER VI.

ATMOSPHERIC PRESSURE. GENERAL PROPERTIES OF GASES.

The Atmosphere. Atmospheric Pressure.—The atmosphere, or gaseous envelope surrounding the earth, extends to a height of at least 100 miles, and probably, in a very attenuated state, to a much greater distance. The density is greatest at the surface of the earth, and continuously diminishes as the distance from the surface increases. In the higher portions the air is extremely rarefied, the condition being similar to that obtaining in a vacuum-tube. The “aurora borealis” is believed to be due to electric discharges in the higher attenuated portions of the atmosphere.

The gaseous envelope, which is held to the earth by gravitation, exerts a distinct pressure on all objects beneath it. We are not conscious of this pressure on our bodies, owing to the fact that the pressure acts inside the body as well as externally, and the two effects counterbalance. Similarly, a flat surface, such as a table, does not show any sign of the presence of this pressure, as, owing to the property possessed by fluids of pressing equally in all directions, the upward pressure beneath the table balances that on the upper surface. To demonstrate the existence of this pressure, it is necessary to remove the balancing pressure, which may be done in many ways. If a rubber disk be stretched tightly over the mouth of a jar, and the air be removed from the jar, the rubber will be forced into the interior, and may even burst owing to the pressure upon it, which is now unbalanced. A thin glass vessel will break when exhausted of air, and a thin metal vessel will be crushed inwards. As this pressure is always present, and plays an important part in many phenomena, a knowledge of its numerical amount is of great importance, and is measured by the instrument known as the barometer.

The Mercury Barometer.—The first mercury barometer was constructed by Torricelli, who took a tube about 1 yard long and $\frac{1}{2}$ of an inch in diameter and closed at one end. This was completely filled with mercury and closed with the finger, and then inverted and the open end immersed in a cistern of mercury before removing the

finger. The column of mercury which remained in the tube, was found to have a vertical height of about 30 inches, the height being measured above the mercury surface in the cistern. This column is sustained by the pressure of the atmosphere, which is transmitted through the mercury in the cistern; and if the whole arrangement be placed in an air-pump receiver, and the air be exhausted completely, the mercury in the tube will fall until it stands level with that in the cistern. On again admitting air to the receiver, the column will rise to its former height.

A simple barometer of this kind is shown in Fig. 23; and it should be carefully remembered that the atmospheric pressure balances the column of mercury above the cistern level, and not the



FIG. 23.
SIMPLE
BAROMETER.

entire length, for if the top of the barometer were broken, the pressure of the atmosphere would cause the column to fall until the level was the same in both tube and cistern, and no further. In making a good barometer both the tube and the mercury should be scrupulously clean, and every trace of air removed from the mercury and tube by boiling, either at ordinary pressure or when attached to an air-pump. Any tangible quantity of air left in the tube causes a noticeable depression of the column, and therefore an erroneous reading. When inclined, the mercury should completely fill the tube, and on sudden tilting, should strike the glass with a metallic sound. If well made, the space at the top of the column, known as the Torricellian vacuum, should contain only mercury vapour.

On ascending, the weight of the overlying column of air becomes continuously less, and consequently the length of the column of mercury in the barometer falls. At an elevation of 1000 feet, for example, the height of the barometer is about 1 inch less than it would be if at sea-level. The height of the column of mercury, like the density of the atmosphere, falls in a diminishing ratio as the distance from the surface of the earth increases; and would become zero at the upper limit of the atmosphere. If the atmosphere were of the same density throughout as that existing at the surface, a height of 5 miles would suffice to hold up the mercury in the barometer, and uniform decrease would be observed on ascending. It is customary to speak of the atmosphere, on the supposition of uniform density, as the "homogeneous atmosphere"; but it

should be remembered that in reality the density decreases with the height.

The average height of the barometer at sea-level is approximately 76 centimetres or 29·92 inches. The height is constantly fluctuating owing to alterations in the amount of moisture present in the atmosphere, winds, etc. A low barometer (*i.e.*, when the reading is much below 29 inches or 73·5 centimetres) is usually accompanied by rain and atmospheric disturbances, whilst a high barometer (30 inches and over) is generally associated with dry weather and calm conditions. In Britain the barometer seldom falls below 28·5 inches, or 72·4 centimetres; or rises above 30·8 inches or 78·2 centimetres. As it is desirable for meteorological and other purposes, to obtain exact readings of the height of the barometer, special instruments, fitted with verniers for fine readings, are employed. The form in common use, known as Fortin's barometer, will now be described.

Fortin's Barometer.—In any mercury barometer the level in the cistern will, of necessity, alter when the column of mercury rises or falls. In the one case, mercury from the cistern enters the tube, and in the other case mercury leaves the tube and enters the cistern. As the height to be measured is the distance between the top of the column and the mercury surface in the cistern, it is evident that a fixed scale would give erroneous readings unless provision were made for the varying level in the cistern. This is accomplished in Fortin's barometer by making the lower portion of the cistern of leather; and by means of a screw this can be raised or lowered until the mercury surface just touches a fixed ivory peg, which has a sharp point. Exact contact is insured when the point of the peg appears just to meet its own reflection in the mercury. The scale is fixed so that the heights indicated represent the distance from the point of the ivory peg. The mercury in the cistern is adjusted to this point before a reading is taken, and thus any error due to altering level is eliminated. A sliding vernier, reading to $\frac{1}{500}$ of an inch, or to $\frac{1}{200}$ of a centimetre, is adjusted to the top of the column, and an exact reading is thus obtained.

Corrections of Barometer Readings.—In order that barometer readings, taken under different circumstances, may be strictly comparable, it is necessary to define standard conditions under which the height is recorded. The chief causes which affect the reading are temperature and elevation above sea-level, and to secure uniformity the observed height is corrected so as to represent what the reading would be if the temperature were 0° C. and the barometer at sea-level. The correction for temperature is obtained from the known coefficients of

expansion of mercury and the material of the scale. With a brass scale, the correction is made from the expression

$$\text{Height at } 0^{\circ} \text{ C.} = \text{height at } t^{\circ} \text{ C.} \times (1 - .000162 t),$$

where .000162 is the difference between the coefficient of absolute expansion of mercury (.000181), and the linear coefficient of brass (.000019). For accurate observation of the temperature, a thermometer is fastened to the barometer.

Example.—The observed height of the barometer is 765 mm., the temperature being 20° C. The corrected height is therefore

$$\begin{aligned} H_0 &= H \text{ at } 20^{\circ} \times \{1 - (20 \times .000162)\} \\ &= 765 \times .99676 \\ &= 762.6 \text{ mm.} \end{aligned}$$

The correction for elevation may be made by referring to tables prepared for the purpose, in which the alteration of barometric pressure due to altitude, under given conditions of temperature, moisture, etc. is recorded. For rough purposes, $\frac{1}{10}$ of an inch may be added for every 100 feet of elevation, up to 1000 feet. Other corrections, though of less general importance, are for capillarity and latitude, the latter being necessary when the barometer is transferred to a locality in which the value of "g" differs sensibly, as this would cause an alteration in the downward pressure exerted by a given column of mercury.

"Standard" or "Normal" Barometric Pressure.—The standard pressure to which the volumes of gases and also their densities are referred is 760 millimetres of mercury at 0° C. This is equal to 29.92 inches; and such a column of mercury is said to represent 1 "atmosphere" of pressure. The equivalent of 1 atmosphere is 1033.3 grams per square centimetre, or 14.7 lb. per square inch.

Example.—A tube of 1 square centimetre section, in which the mercury stands at a height of 76 centimetres, will contain 76 c.c. of mercury. As 1 c.c. of mercury at 0° C. weighs 13.596 grams, the pressure per square centimetre = weight of mercury in tube = $76 \times 13.596 = 1033.3$ grams. Similarly, 29.92 cubic inches of mercury weigh 14.7 lb., and the pressure per square inch = 14.7 lb. A column of mercury 1 inch high represents a pressure of .4913 lb. per square inch, as 1 cubic inch of mercury weighs .4913 lb. A pressure of 1 lb. per square inch is represented by a column of mercury $\frac{1}{.4913} = 2.038$ inches high.

Aneroid Barometers.—The chief drawback to the general use of the mercury barometer is its lack of portability. Apart from the length, which must be about 1 yard at a minimum, there is always a danger of the mercury spilling, or the tube being broken except when the greatest care is exercised in transit. These disadvantages are not shared by the aneroid barometer, which depends for its action on the upward or downward movement of the surface of an exhausted metallic drum under fluctuations of atmospheric pressure. This drum has a corrugated surface, and in the usual form is kept in a state of extension by a steel spring; the lower end of the drum being fastened to a plate, whilst the upper end is free to move. The movements of the upper surface are communicated by means of multiplying levers to a chain which passes round the spindle carrying the index. An increase in the barometric pressure causes the upper end of the drum to collapse by a definite amount, with the result that the index hand moves over the scale. A decrease in barometric pressure enables the spring to extend the drum, and the movement being conveyed to the index, causes a converse motion to that which results from increased pressure. The chain is prevented from becoming slack by means of a hair-spring. The correct markings on the scale over which the index moves are obtained by comparison with a mercury barometer.

A well-made aneroid barometer, which has been carefully graduated, and the various parts compensated for temperature, is susceptible of very great accuracy. In size aneroid barometers vary from that of an ordinary watch to a diameter of 9 or 10 inches, the former being intended for carrying in the pocket, and the latter for a fixed position, to replace an ordinary barometer. The smaller sizes are usually provided with a scale of heights on the face of the instrument, so that elevations may be read off at a glance. For rough surveys and contouring this form of barometer is greatly superior to the mercury barometer, as it is no trouble to carry, and cannot get out of order with ordinary usage.

The aneroid principle is also adopted in certain forms of "barographs," or recording barometers. Several drums are mounted on the same spindle, so as to give an increased effect, and the terminal lever carries a pen, which is in contact with a paper moved by clockwork. The pen is set at the correct height on the paper by comparison with a mercury barometer; and as the clockwork revolves at a known rate it is possible to obtain a continuous record of atmospheric pressure.

States of Matter—Kinetic Theory—Special Properties of Matter in

II

the Gaseous State.—It is customary to refer to matter as existing in three well-defined states—the solid, the liquid, and the gaseous. It is possible, however, for matter to exist in a transitional state between solid and liquid, or between liquid and gas, as will be shown later in connection with the phenomena attending change of state. A fourth, or ultra-gaseous state of matter, is realised in vacuum tubes, in which the residual matter possesses properties entirely different from those of a gas under ordinary pressures.

According to the Kinetic theory, the molecules of which all kinds of matter are composed are in a constant state of motion. In a solid, the motion is restricted to the space between a given molecule and those which surround it, so that each molecule is confined to a small area out of which it cannot escape. A much greater freedom of motion obtains in a liquid, as in this case the molecules are able to wander amongst neighbouring molecules. Finally, in the gaseous state, the molecules are free to move in all directions, practically unhindered by the presence of adjacent molecules. This view of the condition of matter in its various forms is not only in harmony with experimental results in general, but is supported by direct evidence. The phenomenon of diffusion, in particular, lends confirmation to the theory of molecular motion. If a light liquid be allowed to float on a heavy one, it will generally be found that after the lapse of some hours a quantity of the heavy liquid has mingled with the lighter one, and *vice versa*. Similarly, a light gas, such as hydrogen, if contained in a cylinder and placed upon a cylinder containing a heavy gas, such as sulphur dioxide, will penetrate the lower cylinder almost immediately, the heavier gas similarly rising into the hydrogen cylinder. This mixing in opposition to gravitation is explained satisfactorily by the Kinetic theory; the comparatively slow diffusion of the liquids being due to the difficulty experienced by the molecules in moving between other molecules, and the rapid mixing of gases by the practically complete freedom of motion. Roberts-Austen has shown that diffusion may occur with solids, though extremely slowly. A block of lead was allowed to stand for some months on a block of gold, after which it was found that some of the gold had passed upwards into the lead, and conversely. It would appear, therefore, that even in solids a molecule is not absolutely hemmed in by its neighbours, but may—though with extreme difficulty—move between them.

Gases differ from liquids and solids by possessing the property of indefinite expansion. No matter what proportion of a gas is withdrawn from a vessel, the residue, however small, distributes itself

evenly through the vessel, and in this sense fills it. A liquid, on the other hand, possesses a boundary surface, which defines its volume. A gas has no boundaries save the walls of the containing vessel, and the smallest quantity of gas appears to be capable of filling (in the sense of even distribution) any vessel, however large.

Gaseous Pressure.—Gases exert a pressure on all the parts of the containing vessel, which is equally distributed over the whole surface. The existence of this pressure may be shown by taking a jar covered with a rubber disk, and removing the surrounding air by placing the jar under the receiver of an air-pump, when the rubber disk will be observed to stretch into a hemisphere under the pressure of the enclosed air. This pressure, according to the Kinetic theory, is due to the continuous impact of the molecules of the gas on the walls of the vessel. After striking the vessel the molecules rebound, and may collide with each other, but as all the molecules are constantly in a state of rapid motion a continuous series of impacts on the walls of the vessel will occur. The pressure to which these impacts give rise will evidently depend upon the mass, velocity, and number of molecules striking in a given time. If the number of molecules be doubled (by forcing into the vessel a further quantity of gas equal to its original contents) the pressure will be doubled; and conversely, removing one-half of the gas, or increasing two-fold the area of the vessel, will cause the pressure to be halved. An increase in velocity, such as is caused by a rise of temperature, will cause an increase of pressure. All these conclusions may be verified by experiment.

Adopting this view of gaseous pressure, it will be seen that a gas confined beneath a piston on which weights are placed will accommodate its volume until the pressure beneath the piston is equal to that caused by the weights above. As the gas diminishes in volume, the area over which impacts are delivered by the molecules also diminishes, and the piston is struck by a greater number of molecules in a given time. Finally, the combined force of the impacts is just sufficient to counterbalance the weight, and the volume of the gas remains stationary. This explanation leads to the conclusion that the pressure exerted by a given mass of gas (at constant temperature) should vary inversely as the volume occupied—which is equivalent to Boyle's law.

Connection between Gaseous Volume and Pressure. Boyle's Law.—The effect of varying the pressure on a given mass of air was first investigated by Robert Boyle, in 1660. Boyle found that the volume of the air varied in the inverse ratio of the pressure within the limit of four atmospheres. Later experiments showed that the law could

be extended to other gases, within certain limits; and in the case of hydrogen, nitrogen, air and oxygen, the law was found to be closely followed, even at considerably higher pressures than were employed by Boyle. The useful law deduced from these experiments, is known as Boyle's law, and may be stated thus: "The volume occupied by a given mass of gas, at constant temperature, varies inversely as the pressure to which it is subjected." If the pressure be doubled, the volume is halved, or, in general, the product of pressure and volume is constant for a given mass of gas. Expressed in symbols, $PV = \text{a constant}$; or $PV = P_1 V_1$ where P and V are original and P_1 and V_1 the altered pressure and volume.

More exact experiments by Regnault, Amagat, and others have shown that no known gas obeys Boyle's law exactly. In general, the product PV at first diminishes with increase of pressure until a minimum value is attained; after which the value of PV increases. The variations of PV depend also upon the temperature at which the experiment is conducted. If the temperature be near that at which the gas liquefies, the product PV is far less than is demanded by the law as the pressure increases. Easily liquefied gases, such as sulphur-dioxide and ammonia, therefore show a marked departure from Boyle's law, even when subjected to moderate pressures at ordinary temperatures. At high temperatures these gases approximate closely to the law, and in general the value of PV only approaches a constant value when the gas is considerably above the temperature at which it would liquefy at atmospheric pressure. These discrepancies are explained by the facts that the size of the molecules is not negligible compared with the spaces between them, and that the tendency of molecules to adhere to one another becomes marked as liquefaction approaches. At very low pressures, when the molecules are widely separated, gases might be expected to obey the law almost exactly, and this has been confirmed experimentally by Lord Rayleigh.

Isothermals. Work done in Compressing a Gas Isothermally.—If a substance, kept at a constant temperature throughout, be subjected to a continuous pressure, the volume will undergo a continuous diminution, and a curve drawn connecting pressures with the corresponding volumes is known as the *isothermal* for the substance. Isothermals may have various shapes, depending upon the substance operated on, but in the case of a gas which is assumed to obey Boyle's law accurately, the curve takes the form of a rectangular hyperbola. This is shown in Fig. 24, in which a gas originally occupying a volume represented by ON , is compressed to a volume OL , the continuous change of pressure being exhibited by the curve $KFBM$. From

Boyle's law it follows that the product of pressure and corresponding volume is constant, thus $OC \times CB = OG \times GF$, and, in general, $PV = a \text{ constant}$. The curve possessing this property is an equilateral hyperbola.

The isothermals of a solid, liquid, or vapour may differ widely in shape from those of a gas, and it should be remembered that in all isothermals the temperature is presumed to be constant throughout. This might be realised experimentally by surrounding the substance with ice or a large bath, and increasing the pressure gradually.

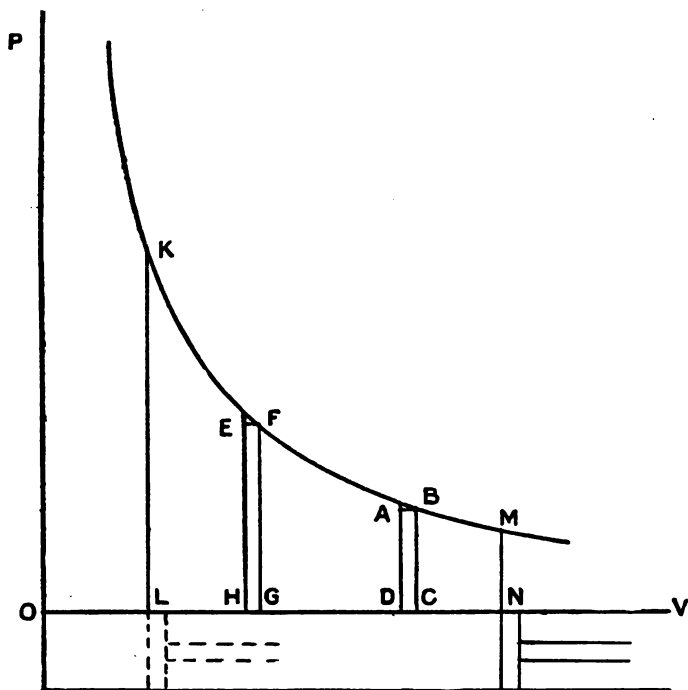


FIG. 24.—ISOTHERMAL OF A PERFECT GAS.

The work done during an isothermal compression is represented by the area of the figure enclosed by the curve, the perpendiculars from the extremities of the curve, and the axis of volume. In Fig. 24, in which the gas is assumed to be compressed isothermally from a volume ON to a volume OL , the starting pressure being represented by NM and the final by LK , the work done is expressed by the area $KLNM$. This may be proved by considering the work

done during a very small part of the compression, as from C to D. Since the work done is the total force applied \times distance moved, and since the total force is equal to the area of the piston \times pressure per unit area, it follows that the work done equals

$$(\text{area of piston} \times \text{pressure per unit area} \times \text{distance moved})$$

But (area of piston \times distance moved) = diminution in volume, hence
work done = (pressure per unit area \times decrease in volume)

$$= P \times CD = P dv.$$

In the figure the work done in compressing from C to D is the area of the rectangle A B C D + the small triangle bounded by A B and the curve. If C and D be separated only by an indefinitely small distance, dv , the triangle vanishes, leaving the rectangle $P dv$. The area K L N M may be imagined to be composed of an indefinite number of such rectangles, and if the areas of all these be added together, the result will be the area K L N M. Or,

$$\text{Work done} = \sum P dv, \text{ or } \int P dv,$$

between the limits O N and O L. Calling O N v_1 , and O L v_2 the total area is found by integration to be

$$p_1 v_1 \times \text{hyp. log } \frac{v_1}{v_2};$$

or, in ordinary logarithms

$$p_1 v_1 \times 2.302585 \times \log \frac{v_1}{v_2};$$

where p_1 and v_1 are the original pressure and volume respectively.

Example 1. If 2.5 cubic feet of air, at a pressure of 14.7 lb. per square inch, be compressed under isothermal conditions to a volume of 0.5 cubic foot, the work done will be

$$2.5 \times (144 \times 14.7) \times 2.302585 \times \log \frac{2.5}{0.5} = 8526 \text{ foot-pounds.}$$

Note that when the answer is in terms of the foot and pound, the original pressure p_1 must be expressed in pounds per square foot = (14.7×144) .

Example 2. On compressing 1 litre of air, originally at a pressure of 1000 grams per square centimetre, to a volume of 100 c.c., under isothermal conditions, the work done would be

$$1000 \times 1000 \times 2.302585 \times \log \frac{1000}{100};$$

$$= 2,302,585 \text{ gram-centimetres; since 1 litre} = 1000 \text{ cubic centimetres.}$$

Connection between Gaseous Volume and Temperature. Charles' Law. Absolute Zero.—It has been pointed out previously that the increase in volume observed when a quantity of gas is heated at constant pressure, is uniform; the increase per degree C. being $\frac{1}{273}$ of the volume occupied by the gas at 0° C. Experiment has shown that this value holds nearly true for all gases, within certain limits. As in the case of Boyle's law, however, gases near the temperature of liquefaction show a marked deviation from the above figure. For all ordinary calculations involving the volume changes of gases at constant pressure, it is sufficiently accurate to assume the figure $\frac{1}{273}$, or 0.003663, as representing the coefficient of expansion of a gas. This connection between volume and temperature is known as Charles' law, and may be expressed in symbols as follows:—

$$V_1 = V_0 (1 + \alpha t_1) \quad . \quad . \quad . \quad (1)$$

where V_1 = volume at t_1° ; V_0 = volume at 0° C.; and α = the coefficient of expansion = $\frac{1}{273}$. From this expression the ratio of the volumes at any two temperatures may be obtained, as it follows that

$$V_2 = V_0 (1 + \alpha t_2) \quad . \quad . \quad . \quad (2)$$

Dividing (1) by (2), the relation becomes

$$\frac{V_1}{V_2} = \frac{1 + \alpha t_1}{1 + \alpha t_2}$$

If a gas be cooled below 0° C., the contraction is still found to be $\frac{1}{273}$ of the volume at 0° C. for every degree through which it is cooled, and, consequently, if a gas could be cooled to a temperature of -273° C., its volume, on the assumption that the law held true, should become zero. Thus 273 volumes of gas at 0° C. would become 272 at -1° ; 173 at -100° , and nothing at -273° . It cannot be imagined that any form of matter could occupy no volume, and consequently some deviation from the law would occur as the temperature of -273° C. was approached, even with a gas that showed no signs of liquefaction. There is, however, another method of regarding the properties of gases at this temperature. If a gas be heated without being allowed to expand, the pressure rises by $\frac{1}{273}$ of the pressure

at 0°C. for each degree rise of temperature, and similarly decreases on contracting without change of volume. Thus, if the pressure at 0°C. were 760 mm., at 273° it would become 1520 mm., and would vanish at -273° . At this temperature, therefore, a gas could not exert pressure, and, consequently, its molecules would be at rest. In other words, the distinctive gaseous properties would have disappeared, and consequently, the laws of Boyle and Charles could no longer be applied to it. So long as the gas possesses heat energy the molecules will be in a state of motion, and therefore it follows that at -273°C. , at which temperature the molecules are at rest, the gas has been deprived of all its heat. For this reason, the temperature -273°C. (or -459.4°F.), is called the *absolute zero* of temperature. Absolute temperatures, on the Centigrade scale, are therefore 273° higher than the ordinary degrees; thus $10^{\circ}\text{C.} = 283^{\circ}$ absolute, and so on.

The law of Charles may be simply expressed in terms of absolute degrees as follows:—The volume occupied by a gas at constant pressure is proportional to its absolute temperature. Or, in symbols,

$$\frac{V}{T} = \frac{V_1}{T_1}.$$

V and T representing original, and V_1 and T_1 final, volume and *absolute* temperature respectively. This method of expressing the law is more convenient for the purposes of calculation.

Combination of Boyle's and Charles' Laws.—Boyle's law assumes that a gas remains at constant temperature whilst altering its pressure, and Charles' law assumes constant pressure. If both the temperature and pressure alter, a combination of the two laws is necessary to calculate the volume. This may be obtained as follows:—

Let V , P , and T represent the initial, and V_1 , P_1 , and T_1 , the final volume, pressure, and absolute temperature of a gas. Then, considering temperatures only,

$$V_1 \text{ would equal } V \times \frac{T_1}{T},$$

but as the pressure alters also, the final value will be

$$V_1 = V \times \frac{T_1}{T} \times \frac{P}{P_1},$$

from which

$$\frac{P V}{T} = \frac{P_1 V_1}{T_1},$$

which expression may be used in all cases concerning the alteration in volume of a gas. If $T = T_1$, the expression is identical with Boyle's law; if $P = P_1$, Charles' law is expressed as given above. The equation may be written in the form

$$PV = RT,$$

where R is a constant. A few examples to illustrate the application of the laws will now be given.

Examples.—(1) 500 cubic feet of gas at 7°C. and 750 mm. pressure, are heated to 127°C. , and the pressure allowed to rise to 800 mm. Find the volume of the gas under the new conditions.

Applying in the formula

$$\frac{PV}{T} = \frac{P_1 V_1}{T_1},$$

$$\frac{750 \times 500}{280} = \frac{800 \times V_1}{400}$$

from which $V_1 = 669.6$ cubic feet. (Note that 273 is added to the given temperatures to give absolute degrees.)

(2) A mass of gas, originally at 15°C. , is heated in a closed vessel to 500°C. Assuming the original pressure to have been 1 atmosphere, find the final pressure.

In this case $V = V_1$, and the expression becomes

$$\frac{P}{T} = \frac{P_1}{T_1}, \quad \therefore \frac{1}{288} = \frac{P_1}{773},$$

from which $P_1 = 2.68$ atmospheres.

(3) A closed glass bulb contains air at 0°C. , and 750 mm. pressure. On placing in a bath the additional pressure exerted is 1000 mm. Find the temperature of the bath.

Since $V = V_1$,

$$\frac{P}{T} = \frac{P_1}{T_1},$$

therefore

$$\frac{750}{273} = \frac{(1000 + 750)}{T_1}$$

and $T_1 = 637^\circ$ absolute, or 364°C.

Heat Produced by the Compression of Gases.—The compression of a gas causes a rise in temperature, due to the conversion of work into heat. The fire-syringe depends for its action on the heat produced by the compression of air, and consists of a cylinder fitted with a tight piston, on the under side of which is fastened a piece of tinder. On suddenly plunging down the piston, a rise in temperature takes place sufficient to ignite the tinder. More recently the heat of compression of a gas has been utilised to ignite the charge in certain forms of oil engines; an operation which involves, however, a very high compression of the charge. In a perfect gas, the molecules of which are supposed to be quite independent of each other, the heat produced would be the exact equivalent of the work done in compression, every 1400 ft. lb. of work producing 1 lb.-° C. unit of heat. Conversely, if a compressed gas be allowed to expand, so as to do work, a lowering of temperature is produced, the gas being deprived of 1 lb.-° C. unit of heat for every 1400 ft. lb. of work done by the expanding gas. If the gas expanded into a vacuum, no work would be done, and no fall of temperature would be produced. On expanding into the atmosphere, however, work is done in overcoming the pressure of the overlying air, and a lowering of temperature occurs. If the expanding gas be allowed to perform a greater quantity of work, such as in driving a machine, a greater fall in temperature is caused, this being the principle of refrigerating machines of the air-expansion type. It should be remembered, however, that the work done on the gas during compression, or by the gas during expansion, is the equivalent of the heat produced or extracted provided the molecules of the gas are independent of one another. No ordinary gas, however, is perfect in this sense, and a certain amount of work must be involved in causing the molecules to approach each other, or in dragging them apart—according to whether the molecules repel or attract each other. The work quantity involved on this account, however, is extremely small, as was shown experimentally by Joule.

Joule's Experiments on Expanding Gases.—In investigating this question Joule took two cylinders, connected by a pipe and stopcock. One of the cylinders contained air at 22 atmospheres pressure, and the other was exhausted. Both were immersed in a calorimeter containing water, and the stopcock opened. After stirring the water no alteration of temperature was observed, and consequently no measurable amount of heat was converted into work in causing the molecules of the air to move a greater distance apart from one another, as would be the case if they tended to adhere to each other. In a

second experiment Joule placed the cylinders in separate calorimeters, and opened the stopcock. The expanding gas, by doing work in overcoming the pressure of the gas accumulating in the other cylinder, fell in temperature, whilst a rise in temperature occurred in the case of the gas undergoing compression. It was found that the amount of heat lost by the expansion was balanced by that gained in the compression, showing that in either process the tendency of the molecules to adhere or repel one another was too small to be detected by the experiment. The conclusion to draw from the experiments is that the *internal* work expended during the changes in volume of a gas is, at most, a quantity too small to be noticed by the methods adopted, and which may be neglected in all ordinary calculations. That mutual attractions between molecules do exist, however, is shown by other experiments, and a method of investigating the matter in question was devised by Joule and Kelvin, which will now be described.

Joule and Kelvin's "Porous Plug" Experiment.—In this experiment a compressed gas was allowed to pass through a spiral surrounded by water at a constant temperature, and afterwards to escape through a glass tube in which a plug of cotton wool was placed. By this means it is possible to maintain a considerable difference of pressure between the sides of the plug, just as in the case of a gas escaping through a fine jet into the air; and the molecules of the gas, after leaving the plug, would separate to a greater distance. A thermometer was placed in the glass tube just beyond the porous plug, and in the case of air and carbon dioxide the escaping gas was found to have a lower temperature than that of the bath, whilst with hydrogen a rise of temperature was observed. In the experiment the cooling due to the expansion of the main mass of the gas was eliminated by the surrounding bath of water, and any cooling on the part of the emerging gas must have been due to the conversion of heat into internal work. The external work is performed by the main mass of the gas (which is prevented by the bath from cooling), and not by the escaping gas. Hence, if the escaping gas were perfect, in the sense that the molecules were independent, and that it obeyed Boyle's law accurately, its temperature should undergo no alteration. The greater the departure from perfect conditions, the greater should be the thermal effect, and this is what is actually observed.

Joule and Kelvin found that the alteration in temperature was proportional to the difference of pressure on the two sides of the plug. In the case of air at 0° C. the fall in temperature observed

was 0.29° C. for each atmosphere difference of pressure; for carbon dioxide, 1.25° C.; and for hydrogen a rise of 0.039° C. If the experiment be carried out below -90° C., however, hydrogen shows a cooling effect like other gases.

In the above explanation it has been assumed that the whole of the thermal effect is due to the separation of the molecules. In reality, however, deviation from Boyle's law, and consequent alterations in the value of the product, PV , at the different pressures, also exercise a thermal effect, which, in the case of hydrogen, tends to cause a rise in temperature, and suffices to overcome the cooling due to the separation of its molecules. In other cases the alterations in PV are such as to assist the cooling action.

The cooling of gases occasioned by passing through a plug or jet is now utilised in the liquefaction of air, hydrogen, and other gases, as will subsequently be described.

Adiabatic Compression and Expansion.—Boyle's law applies only to gases compressed or expanded at constant temperature, or isothermally. Such a condition would be realised by slowly altering the volume of a gas in a copper cylinder surrounded by a bath kept at a constant temperature. If, however, the gas were contained in a cylinder made of non-conducting material, and suddenly compressed, the heat produced by the compression would not escape, but, by raising the temperature of the gas, would tend to cause expansion and so oppose the pressure. If the alteration in volume takes place in such a manner that heat neither leaves nor enters the gas, the change is called "adiabatic." If a curve be drawn connecting pressure and volume during an adiabatic compression, it will be steeper than the isothermal commencing at the same point, as shown in Fig. 25. For, in the case of the adiabatic, a greater pressure must be applied to produce a given diminution in volume, as the heat generated remains in the gas and increases its pressure. Perfect adiabatic conditions cannot be obtained in practice, but fairly close approximations occur in the operations of heat engines. It may be added that the term "adiabatic" may be applied equally to solids or liquids.

The equation to an adiabatic curve is

$$PV^{\gamma} = \text{a constant,}$$

or

$$PV^{\gamma} = P_1V_1^{\gamma},$$

where P and V are the original and P_1 and V_1 the final pressures and volumes, and γ the ratio of the specific heat at constant pressure to

that at constant volume, or $\frac{C_p}{C_v}$. For gases difficult to liquefy the value of γ is about 1.4. The proof of this equation may be found in theoretical treatises.

The value of γ for a given gas may be found in several ways. One method, by which the figure may be deduced from considerations of

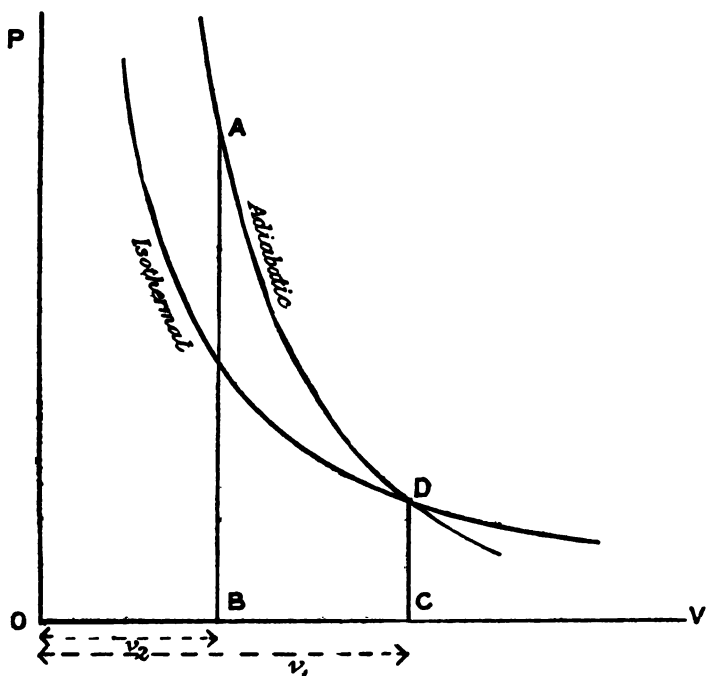


FIG. 25.—ISOTHERMAL AND ADIABATIC OF A GAS.

the velocity of sound, will not be gone into here. The introduction of the steam calorimeter by Joly has enabled the specific heat of a gas at constant volume to be obtained experimentally, which was not possible by any previous method. As the specific heat at constant pressure may also be determined, the ratio γ can be found by direct experiments on the individual specific heats. Before Joly's method was known, however, an experimental method was devised by Clement and Desorme for obtaining the value of γ , and from this value calculating the specific heat at constant volume. A large glass globe, furnished with a tap of wide bore, and also with a gauge-tube

containing a light liquid for noting small alterations in the internal pressure, is filled with air at a slightly reduced pressure. On opening the tap air rushes in, and the pressure rises to that of the atmosphere. The air originally in the globe thereby undergoes compression, and its temperature therefore rises. If the tap be closed rapidly, the air in the globe will cool, and the pressure will fall below atmospheric, but not so much below as initially, as more air is now in the globe. If the compression of the gas be performed rapidly by the sudden opening of the wide-bore tap, it may be regarded as an adiabatic compression, and the value of γ may be calculated from the three observed pressures as under:—

Let P = the atmospheric pressure ;

P_1 = pressure inside the globe before opening the tap (= P - height of liquid in gauge reduced to mercury equivalent) ;

P_2 = pressure inside globe after cooling to the original temperature.

Then, considering the compression as adiabatic, the pressure and volume of the enclosed gas before and after opening the tap will be represented by

$$P_1 V_1^\gamma = P V^\gamma.$$

Taking logarithms, this becomes

$$\gamma (\log V_1 - \log V) = \log P - \log P_1 \quad . \quad . \quad (1)$$

If the temperature at the final reading of the gauge is equal to that at the beginning, then, from Boyle's law,

$$P_1 V_1 = P_2 V,$$

and

$$\frac{V_1}{V} = \frac{P_2}{P_1} \quad . \quad . \quad . \quad (2)$$

Writing equation (1) in the form

$$\gamma \left(\log \frac{V_1}{V} \right) = \log \frac{P}{P_1},$$

and substituting

$$\frac{P_2}{P_1} \text{ for } \frac{V_1}{V},$$

$$\gamma = \frac{\log P - \log P_1}{\log P_2 - \log P_1}.$$

Hence the value of γ may be obtained by the observation of the three pressures.

Other methods may also be adopted for finding the ratio of the two specific heats. The value of γ for a number of gases and vapours is appended :

Substance	$\frac{C_p}{C_v} = \gamma$
Air	1.410
Oxygen	1.402
Nitrogen	1.412
Hydrogen	1.414
Ammonia	1.370
Carbon dioxide	1.261
Steam	1.298
Sulphur dioxide	1.265

Calculation of Rise of Temperature due to Adiabatic Compression.—

The equation connecting the volume and pressure of a gas when compressed without loss or gain of heat is

$$P V^\gamma = P_1 V_1^\gamma \quad . \quad . \quad . \quad . \quad (1)$$

and from this the volume occupied by the gas after being raised to a definite pressure may be calculated, and similarly the pressure produced by a given reduction of volume. To obtain the temperature resulting from the compression, the above equation must be combined with the general equation to a gas, viz.

$$\frac{P V}{T} = \frac{P_1 V_1}{T_1} \quad . \quad . \quad . \quad . \quad (2)$$

Thus from (1)

$$\frac{P}{P_1} = \left(\frac{V_1}{V}\right)^\gamma \text{ and } \frac{V}{V_1} = \left(\frac{P_1}{P}\right)^{\frac{1}{\gamma}},$$

and from (2)

$$\frac{T_1}{T} = \frac{P_1}{P} \times \frac{V_1}{V}.$$

Substituting in (2) the value of $\frac{P_1}{P}$ in terms of V and V_1 , we have

$$\frac{T_1}{T} = \frac{V_1}{V} \times \left(\frac{V}{V_1}\right)^{\gamma} = \left(\frac{V}{V_1}\right)^{\gamma-1}$$

$$\therefore T_1 = T \times \left(\frac{V}{V_1}\right)^{\gamma-1} \quad . \quad . \quad . \quad (3)$$

Similarly, by substituting in (2) the value of $\frac{V_1}{V}$ in terms of P_1 and P , we have

$$T_1 = T \times \left(\frac{P_1}{P}\right)^{\frac{\gamma-1}{\gamma}} \quad . \quad . \quad . \quad (4)$$

The above substitutions are conducted according to the theory of indices, which must be understood in order to follow them. Examples of the use of the formula will now be given.

Example 1.—20 cubic feet of air, at 15° C. and 14.7 lb. pressure, are suddenly compressed to 5 cubic feet, all the heat remaining in the gas. Find the temperature of the air after compression.

$$\gamma \text{ (for air} = 1.41).$$

From equation (3)

$$\therefore T_1 = T \times \left(\frac{20}{5}\right)^{0.41}$$

but $T = 288^\circ$ absolute,

$$\therefore T_1 = 288 \times (5)^{0.41}$$

$$\therefore T_1 = 506^\circ \text{ absolute nearly}$$

$$\text{or} \quad 506 - 273 = 233^\circ \text{ C.}$$

Example 2.—The ignition point of a mixture of gases is 550° C. If the mixture be originally at 20° C. and normal atmospheric pressure, find the pressure at the moment of ignition when the temperature is raised by an adiabatic compression, assuming that $\gamma = 1.41$.

From equation (4)

$$(550 + 273) = 293 \times \left(\frac{P_1}{1}\right)^{\frac{0.41}{1.41}}$$

$$\therefore 823 = 293 \times (P_1)^{0.291}$$

$$\therefore P_1 = 34.75 \text{ atmospheres.}$$

The calculation of the cooling effect produced by an adiabatic expansion is not so simple, and will obviously depend upon the

amount of work done by the expanding gas. The work done in an adiabatic compression is represented, as in the case of an isothermal, by the area bounded by the curve, the ordinates representing the initial and final pressures, and the axis of volume. In Fig. 25, for example, the work done in compressing a gas adiabatically from a volume v_1 to a volume v_2 , is represented by the area A B C D, and is definite for a given compression. By integration the work done may be shown to be equal to

$$\left(\frac{p_1 v_1 - p_2 v_2}{\gamma - 1} \right),$$

where p_1 is the original, and p_2 the final pressure. On the other hand a compressed gas on expanding from v_2 to v_1 may do so with the performance of varying quantities of external work, according to the arrangement of the experiment. Thus a compressed gas may be confined beneath a piston which is open to the atmosphere on its upper side, in which case the work done by the expanding gas will be that required to overcome the atmospheric pressure only. Again, the piston might be connected to a machine, in which case the expanding gas would do the additional work of driving the machine; or, if a vacuum existed on the upper side of the piston, no work would be done in the expansion save that required to lift the piston itself. The amount of work done by an expanding gas may therefore be varied indefinitely, and the cooling effect which is caused by the conversion of heat stored in the gas into work, will vary in like manner. If it can so be arranged that the expanding gas performs an amount of work equal to that required in producing the compression, the formulæ used in the previous examples may be applied, but not otherwise. Thus, in Fig. 25, a gas compressed from v_1 to v_2 adiabatically involves the performance of work represented by the area A B C D, and undergoes a rise in temperature. If the compressed gas can be arranged to expand again to v_1 so as to perform work equal to the area A B C D during the expansion, the temperature will fall to that which existed at the commencement of the compression. If less work be done, the temperature will not fall to the same extent, and the gas will be hotter at the end of the expansion than it was before compression.

Example.—If air, originally at 10 atmospheres pressure and 20° C. expand to 1 atmosphere, doing work equal to that which would be required to restore it to its original condition, the temperature would be from (4)

$$T_2 = 293 \times \left(\frac{1}{10} \right)^{0.292}$$

$$\therefore T_1 = 149.2^\circ \text{ abs.} = -123.8^\circ \text{ C.}$$

In the cold air refrigerating machine the expanding air does work in helping to drive the machine, so as to assist in compressing the next charge. A very low temperature is thus obtained, -62°C. or -80°F. often being observed.

Mayer's Calculation of the Mechanical Equivalent of Heat from the two Specific Heats of Gases.—In the year 1842, Dr. Julius Mayer published a paper containing a calculation of the value of the mechanical equivalent of heat, based on the assumption that the heat produced in the compression of a gas, or lost during its expansion, is the exact equivalent of work done. The principle of Mayer's calculation is as follows: imagine a cylinder containing air, and fitted with a weightless piston. For simplicity of calculation, suppose the volume of the air beneath the piston to be originally 1 litre; the area of section 100 square centimetres; and the temperature 0°C. The distance between the end of the cylinder and the under side of the piston will then be 10 cm. If the temperature be raised to 273°C. , the volume of air, by Charles' law, will be doubled, and the piston will be raised 10 cm. against the pressure of the atmosphere. The number of heat units required in the process may be calculated from a knowledge of the specific heat of air at constant pressure, for, as the piston is free to move, the pressure of the enclosed air will not alter. If, however, the piston be fastened down before heating, the conditions are those of a constant volume, and a smaller amount of heat will be required to raise the temperature of the air to 273°C. The difference between the heat quantities in the two cases was assumed by Mayer to be the exact equivalent of the work done in raising the piston. The calculation, using modern values for the constants for air, may then be made as under:—

Constants for Dry Air.

Weight of 1 litre at 0°C. and 760 mm. = 1.293 gram

Specific heat at constant pressure = .238 "

" " at constant volume = .169 "

Pressure of atmosphere = 760 mm.

= 1033 grams per sq. centimetre.

Calories required to raise temperature from

0°C. to 273°C. at constant pressure = 1.293

$\times 0.238 \times 273$ = 84.03

Ditto at constant volume = 1.293 $\times 0.169 \times$

273 = 59.67

Difference = 24.36

$$\begin{aligned}
 \text{Work done in raising piston} &= \text{total} \\
 &\text{pressure on piston} \times \text{distance} \\
 &\text{moved} = 1033 \times 100 \times 10 = 1,033,000 \text{ cm. grm.} \\
 \text{Equating, } 24 \cdot 36 \text{ calories} &= 1,033,000 \text{ cm. grm.} \\
 \therefore 1 \text{ calorie} &= 42,390 \text{ cm. grm.}
 \end{aligned}$$

The same result will be obtained whatever mass of air, or rise in temperature, be considered; the quantities chosen in the above example are merely for the purpose of simplifying the calculation. Or, if desired, the result may be obtained in British units by a similar process.

The actual figure given by Mayer was 36,700 cm. grm., the error being due to the use of inaccurate data. Moreover, the assumption is made that the whole of the heat is expended in external work, which, as we have seen, is almost, though not quite, correct; but at the time Mayer's calculation was published, no experimental evidence of the truth of the assumption was available. Nor could it be predicted beforehand that the molecules of a gas would require practically no force to drag them apart. Hence, although Mayer's result was published prior to those of Joule, it is to the latter that the credit of first determining the mechanical equivalent of heat is due.

Properties of a "Perfect" Gas.—The laws concerning gases are not exactly obeyed by any known gas, but an ideal gas may be imagined which would exactly conform to these laws under all conditions. A gas, in order to be "perfect," would possess the following properties:—

1. It would obey Boyle's law exactly under all conditions.
2. Its specific heat at constant pressure would be the same at all temperatures and pressures.
3. The external heat required to enable the gas to expand at constant pressure would be the exact equivalent of the work done by the expansion, *i.e.*, there would be an entire absence of internal molecular work.

Of the known gases, hydrogen, helium and nitrogen approximate most closely in properties to those of a perfect gas. A much greater deviation is noticed in the case of easily liquefied gases, such as sulphur dioxide, ammonia and chlorine, which may be regarded as being vapours rather than true gases. The conception of a perfect gas is of great service, in forming a standard of comparison for known gases.

Operations Depending on Gaseous Pressure. Explosives.—In gas, oil and hot-air engines the piston is propelled by the expansive force

exerted by a mass of hot gas, which in the process loses heat equivalent to the amount of work done. The gas, in reality, acts as a medium for the conversion of heat into work; the heat, in gas and oil engines, being furnished by the combustion of the fuel in the cylinder. The properties of steam or other saturated vapour differ entirely from those of a gas, and will be referred to later.

The heat produced by the compression of a gas is made use of in the Diesel engine to ignite the charge in the cylinder. This involves the use of a high working pressure, sufficient to raise the temperature of the charge to the point of ignition, but results in increased efficiency, and renders ignition devices unnecessary.

The class of substances known as explosives owe their power to the generation of a large quantity of gas at a high temperature. If a piece of guncotton, for example, be burnt in an exhausted vessel the amount of gas collected will be found to occupy several hundred times the volume of the guncotton taken. The generation of this mass of gas, at a high temperature, gives rise to an enormous pressure in a closed space, and this pressure constitutes the force of the explosion. The magnitude of the force generated may be realised from the numerical example which follows:—

One gram of an explosive yields 750 c.c. of gas, measured at 0° C. and 760 mm. pressure. The actual temperature of the gas, at the moment of explosion, is 1200° C. To find the pressure exerted immediately after firing 1 gram in a closed space of 2 c.c. The volume occupied by the gas at 1200° C. and 760 mm. (1 atmosphere) pressure, would be

$$\frac{750 \times (1200 + 273)}{273} = 4047 \text{ c.c.}$$

From Boyle's law, if 4047 c.c. of gas at 1 atmosphere pressure, be compressed into a space of 2 c.c., the pressure will become $\frac{4047}{2} = 2023.5$ atmospheres. This is equal to nearly 13.3 tons per square inch. All explosives may be regarded as bodies which possess stored-up energy, which on decomposition, is liberated in the form of heat. The most powerful explosive is therefore the one that disengages the greatest amount of energy.

Absorption of Gases by Porous Solids.—Many solids, particularly those of a porous character, possess the property of absorbing large quantities of gases. Spongy platinum, and in a less degree platinum wire or foil, are capable of absorbing hydrogen and combustible hydrocarbons, the process being attended by the evolution of heat.

If a piece of spongy platinum, or a spiral of fine platinum wire, be held in a jet of hydrogen or coal gas, the heat generated is sufficient to raise the platinum to incandescence, thus causing the jet to ignite. Gas-lighters based on this property of platinum are in common use, as also is an arrangement for procuring a light, in which the platinum is dipped into the interior of an annular wick steeped in spirits, the vapour of which is absorbed, producing incandescence, and so lighting the lamp. Whilst platinum is capable of absorbing a number of gases and vapours, other substances appear to be able to absorb one gas only. Thus the metal palladium absorbs over 600 times its volume of hydrogen, but is inert towards other gases; and similarly molten silver occludes oxygen only, which is expelled at the moment of setting. Powdered magnesium absorbs hydrogen, which, as also in the case of palladium, may be expelled by heating in a vacuum. It is probable that every solid, to some extent, is capable of entangling gases either in its pores or on its surface.

Wood charcoal exercises this power of absorbing gases to an extraordinary degree, particularly when freshly made. Noxious gases such as sulphuretted hydrogen, sulphur dioxide, and ammonia are readily occluded, to an amount equal to many times the volume of the charcoal. It is to this property that the well-known cleansing powers of charcoal, in such processes as filtration, are due. In addition, the main constituents of the atmosphere—oxygen and nitrogen—are readily absorbed. Charcoal made from porous woods, such as willow or alder, if ground up immediately after making, absorbs oxygen so eagerly, and with such generation of heat, that the mass may ignite. Charcoal for making gunpowder is obtained from woods of the type of willow, and to avert the danger of spontaneous ignition the charcoal is kept for at least two weeks before grinding up. The recent experiments of Professor Dewar show that charcoal made from cocoa-nut fibre possesses a greater absorbing power than any other kind, and that the amount of gas absorbed increases enormously when the charcoal is kept at a very low temperature. In one experiment 50 grams of cocoa-nut charcoal were placed in a tube connected to a meter, and immersed in liquid air at -180°C . The air in the tube was absorbed, causing a reduced pressure, owing to which a further quantity of air passed through the meter into the tube, and was in turn absorbed. This continued until 8 litres of air were registered as having passed through the meter into the charcoal. In another experiment a glass tube about 4 feet in length was taken, closed at one end, the closed end being bent into a parallel branch which contained charcoal, and the open end placed under mercury.

On surrounding the charcoal with liquid air, the enclosed air was absorbed so completely that the mercury rose in the tube to a height equal to that of a standard barometer. These experiments show that it is possible to procure vacua, equal, if not superior, to those obtainable with the best mercury pumps, and the process has been tried commercially in the manufacture of vacuum tubes and glow-lamps. The charcoal-absorption method of obtaining vacua is far more expeditious than the mercury pump, which it will doubtless largely supersede as liquid air becomes cheaper to obtain.

Closely connected with this subject is the passage of gases through solids. If a closed platinum tube containing hydrogen be heated to a white heat, it will be found on cooling that the hydrogen has escaped, leaving a vacuum in the interior; thus showing that whereas hydrogen could pass through the hot platinum, air could not, as otherwise air would be found in the tube after cooling. For this reason, as will be referred to under the subject of Pyrometry, hydrogen gas cannot be employed in a gas-pyrometer furnished with a platinum bulb. Iron, at a red heat, is similarly penetrated by carbon monoxide, and this property probably plays an important part in the process of converting iron into steel.

The physical and chemical condition of gases in the interior of solids is still a matter of conjecture. The outward appearance of the solids is not altered, in general, by the absorption of large quantities of gas, as would be the case if an ordinary chemical action took place. On the other hand, the disengagement of heat appears to point to some form of combination occurring, or to some molecular change in the gas; in which latter connection it may be noted that gases, when absorbed in a solid, are frequently more chemically active than when in the free state. Metals in general, when containing an occluded gas, offer a higher resistance to electricity than when in the pure state.

CHAPTER VII.

THE MEASUREMENT OF TEMPERATURE. LIQUID AND GAS
THERMOMETERS.

Definition of Temperature.—Clerk Maxwell has defined temperature as “the thermal state of a body, considered with reference to its power of imparting heat to other bodies.” Higher and lower temperatures are defined as follows:—“If, when two bodies are placed in thermal communication, one loses heat, and the other gains heat, that body which gives out heat is said to have a higher temperature than that which receives heat from it; and if neither body loses or gains heat, they are said to have the same temperature.” The temperature of a body is therefore its thermal condition, and must not be regarded as expressing heat *quantity*. To raise the temperature of a given mass of water through a given interval requires about thirty times as much heat energy as that expended in raising an equal mass of lead through the same interval. The heat *quantity* involved in a given thermal change therefore depends not only on the temperatures, but also on the thermal capacity of the body employed.

Standards of Temperature.—Temperature is measured by reference to certain arbitrary standards, those now universally chosen being the thermal conditions of melting ice, and the steam from water boiling at normal atmospheric pressure. These standards, originally used by Hooke and Sir Isaac Newton, possess the advantages of absolute constancy and simplicity, and enable instruments made in any place to be standardised so as to be identical. Other standards have been used from time to time, but have been abandoned in favour of the more convenient ice and steam.

The difference between the thermal conditions of ice and steam at 760 mm. pressure is called 100° on the Centigrade scale of temperature, the ice point being marked 0°, and the steam point 100°. On the Fahrenheit scale, largely used in Britain and America, the same points are labelled 32° and 212° respectively, the interval being therefore 180°. A third scale, known as Réaumur, is used in Eastern Europe, in which the ice point, as in the Centigrade scale, is called

0°, and the steam point 80°. For scientific purposes the Centigrade scale is now generally employed, as the numbers chosen are more convenient for use in calculations. The importance of specifying a pressure for the steam point is manifest, as the temperature of steam alters considerably with slight variations of pressure; the melting-point of ice, on the contrary, is practically unaffected by ordinary fluctuations in atmospheric pressure.

Principles of Instruments for Measuring Temperature.—In order to measure temperatures between and beyond the fixed points, advantage must be taken of some regular physical change brought about by changes in temperature. Any of the following, for example, if uniform, may be utilised:—

1. The alteration in volume of a liquid or gas.
2. The change of pressure exerted by an enclosed gas or vapour.
3. The variation in length of a bar of metal.
4. The alteration in the electrical resistance of a metal.
5. The varying electromotive force set up at the junction of two different metals.
6. The difference in the quantity of heat radiated by a given surface.

It is essential, however, that the physical change in question shall be uniform, in order to confer the same value to individual degrees of temperature. When this is the case, the change between the ice and steam point can be noted, and $\frac{1}{100}$ part of the change will then correctly represent 1 degree Centigrade, and $\frac{1}{180}$ part 1 degree Fahrenheit. If the change be uniform at temperatures beyond the fixed points also, the value of 1° will be identical on all parts of the scale.

In practice, however, it is not possible to obtain a physical change of absolute constancy. The expansion of certain gases, such as hydrogen and nitrogen, or the increase of pressure exerted by these gases when enclosed, show an extremely close approximation to uniformity at all temperatures well above those at which they liquefy. For a practical standard, therefore, temperatures on the gas scale are taken as a reference for those arrived at by other methods. On the gas scale 1 degree Centigrade may be defined as $\frac{1}{100}$ part of the increase in volume (or pressure, if enclosed) of a given mass of the standard gas when placed in ice and steam at 760 mm. successively. The other physical changes enumerated are all inferior, in point of uniformity, to the volume or pressure changes in a suitable gas, and when used for measuring temperatures exactly must be compared with the gas scale.

In addition to the correctness of the method adopted, the question of practical convenience in use also arises. Any instrument for measuring temperatures should, as far as possible, be portable, easily read, and inexpensive. These considerations render gas thermometers of little service for everyday use, as these instruments lack the practical qualifications mentioned. For all ordinary purposes, up to the temperature of 500°C. , and down to -39°C. , mercury thermometers are by far the most convenient, and, if properly standardised, are sufficiently accurate. Beyond these ranges of temperature, other instruments must be used, each of which, if accuracy is required, should be compared with the gas scale. It will be seen, subsequently, that it is possible, by taking advantage of one or other of the physical changes previously enumerated, to measure temperatures with considerable accuracy between the limits of -260°C. and $+1500^{\circ}\text{C.}$; and, with more doubtful accuracy, to more than 3000°C.

Having regard to the various physical phenomena involved in the different methods of measuring temperatures, and the discrepancies that might arise, it is highly desirable to have some standard of temperature independent of the substance used. This standard is furnished by considerations concerning the conversion of heat into work, and is known as the *thermodynamic scale*. When a perfect engine takes in heat at one temperature and gives it out at another, the quantities of heat which it takes in and gives out are proportional to these temperatures, whatever medium be used in the engine, and the work done is the equivalent of the difference between the quantities taken in and rejected. It is thus possible to define temperature with respect to work-producing power, and so to form a scale independent of any material. If the interval between ice and steam be represented by 100 ideal degrees, as thus deduced, the temperature of melting ice will be $273\cdot13$ of these degrees, and consequently absolute zero will be $-273\cdot13$ thermodynamic degrees. A hydrogen thermometer based on the alteration in pressure or volume of the gas, gives readings practically identical with those of the thermodynamic scale over a considerable range; other gases show deviations from it owing to being less perfect than hydrogen.

The practical forms of instruments for measuring temperatures will now be described.

Liquid-in-Bulb Thermometers.—The increase in volume sustained by a liquid when heated is the basis of the most common method of measuring temperature. A glass bulb, connected to a stem of fine bore, is filled with liquid to such an extent that the end of the liquid column remains in the stem at all temperatures embraced by the

range of the instrument, and the position of the end of the column in the stem is made to indicate the existing temperature. It is evident that the increase in bulk observed represents the apparent or relative expansion of the liquid, and, if the stem is to be equally divided, this expansion should be uniform. For this reason mercury is chosen for most thermometers; other advantages possessed by mercury being the large range of temperature it will indicate, its low thermal capacity and good conductivity, its visibility even in a thin thread, and the fact that it does not cling to the glass. The range of a mercury thermometer is restricted by its freezing point ($-39^{\circ}\text{C.} = -38.2^{\circ}\text{F.}$), and its boiling point ($357^{\circ}\text{C.} = 674.6^{\circ}\text{F.}$), but by special means it is possible to obtain readings as high as 500°C. with mercury. No other ordinary liquid expands so uniformly as mercury, and none is capable of being used over so wide a range. For special purposes, however, other liquids are sometimes employed.

It is now customary to make mercury thermometers with cylindrical bulbs, which are more convenient in practice than spherical bulbs. In order to prevent a possible escape of liquid, or the entry of moisture or dust, the thermometer is sealed at the top, the air having been previously displaced by heating the bulb, thus causing the mercury to expand and drive out the air, and sealing whilst hot. If necessary, the mercury in the bulb may be boiled to insure complete expulsion of air so that, on cooling, the space above the column should contain nothing but mercury vapour. Before proceeding to mark the stem, the thermometer should be put aside for at least six months after filling, as the bulb undergoes a gradual contraction during this period which would render the readings erroneous if the stem were marked immediately after filling. The greater part of this contraction takes place during the first month, and is not complete even after the lapse of years. After six months, however, the alteration is sufficiently small to ignore in ordinary cases.

The lower fixed point is obtained by placing the bulb, and stem as far as the end of the column, in powdered ice contained in a tunnel or vessel which allows the water resulting from the melting of the ice to drain away. When the column is stationary, a mark is made on the stem opposite the end, and is called $0^{\circ}\text{Centigrade}$ or 32°F. The steam point is obtained by surrounding the thermometer and stem with steam from water boiling at atmospheric pressure, the vessel used for this purpose being as shown in Fig. 26. It consists of a copper boiler, on the top of which are placed two concentric cylinders. The inner cylinder is open at the top, and

contains the thermometer; the outer one serves as a steam jacket and has an opening in the side from which the steam escapes. This arrangement insures that the whole of the thermometer attains the temperature of the steam, and gives a constant result at a given pressure which could not be obtained by immersing the thermometer in boiling water. The stem opposite the top of the column is marked temporarily, as this point will only represent 100°C. , or 212°F. , if the barometric pressure is exactly 760 mm. A deviation of ± 26.8 mm. on either side of the standard causes an alteration in the temperature of the steam of $\pm 1^{\circ}\text{C.}$, or $\pm 1.8^{\circ}\text{F.}$ Intermediate variations of pressure cause a proportional alteration in temperature; thus at 750 mm. pressure the temperature of the steam would be $\left(100 - \frac{10}{26.8}\right) = 99.63^{\circ}\text{C.}$, or 211.3°F.

The figure representing the position of the top of the column is thus determined, and the space between the two marks divided into this number of equal parts by a dividing engine. Sometimes the marks are engraved on the stem; in other cases on a separate scale fastened to the stem. For facility in reading, longer marks are made at every 5° , and numbers placed at every 10° , or more frequently if necessary. The divisions are continued geometrically along the stem in both directions beyond the fixed points.

Alcohol is sometimes used instead of mercury, either for cheapness, or for recording temperatures below the freezing-point of mercury, or for thermometers for other special uses. Alcohol has a higher coefficient of expansion than mercury, and consequently a stem of wider bore may be used for a given size of bulb. To render the column visible, the alcohol is coloured with a dye, such as rosaniline. The boiling-point of alcohol is 79°C. , consequently an alcohol thermometer cannot be standardised in steam. It is customary to mark the ice-point in the usual manner, and to obtain the higher temperatures by comparison with a good mercury thermometer. The low freezing

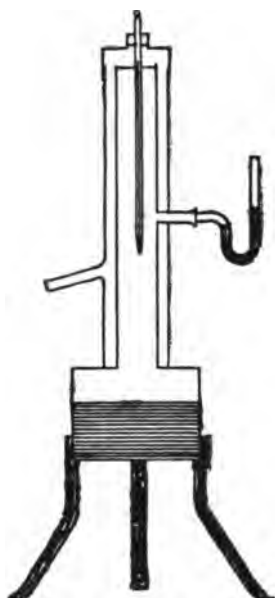


FIG. 26.—METHOD OF OBTAINING THE UPPER FIXED POINT OF A THERMOMETER.

point of alcohol (-112°C.) renders alcohol thermometers of service for observing atmospheric temperatures in the polar regions, where indications far below the freezing-point of mercury are frequently obtained. There appears to be no good reason why turpentine should not be used instead of alcohol for many purposes. It boils at 159°C. , and could therefore be standardised in steam; moreover its expansion in glass is more regular than that of alcohol, though not quite so uniform as that of mercury between 0° and 100° . Turpentine has a coefficient of expansion six times as great as that of mercury, and is cheaper than alcohol, besides possessing the other advantages enumerated.

Thermometers for reading temperatures below the freezing-point of alcohol are now made with pentane (C_5H_{12}) which freezes about -200°C. , and may be used to record temperatures as low as that of liquid air. The use of pentane is restricted to low temperatures, as it boils at 39°C. Such thermometers may be graduated in ice to give one fixed point, and the other points obtained by comparison, in cold media, with a gas thermometer.

Defects of Liquid-in-Bulb Thermometers.—All ordinary thermometers are subject to errors, some of which are inherent, and others avoidable. The markings, if measured accurately, are seldom found to be equidistant; and moreover, it is assumed that the bore of the tube is perfectly cylindrical, which is seldom the case. Errors may also arise from the fixed points being wrongly marked, the author's experience being that, whereas the ice point is usually correct, the steam point may be wrong by $\frac{1}{2}^{\circ}$ or more, owing to the barometric pressure being ignored at the time of marking. Even if these errors were entirely absent, intermediate readings between the fixed points and also beyond, do not agree with those of the gas scale, as mercury in glass does not show a perfectly uniform expansion, and other liquids deviate even more. Thus a mercury thermometer, made of ordinary glass, differs from a gas thermometer by $+0.3^{\circ}$ at 50°C. , -0.2° at 150°C. , -0.3° at 200°C. , $+0.05^{\circ}$ at 250°C. , $+1.08^{\circ}$ at 300°C. , and $+4^{\circ}$ at 350°C. If contained in a non-expansive envelope the differences would be much greater, but, by a fortunate coincidence the varying expansion of the glass bulb, up to 250°C. , nearly neutralises the increased expansion of the mercury. With other kinds of glass the discrepancies are usually greater. If exact readings are required with a given thermometer, it should be sent to the National Physical Laboratory to be compared with the standard instruments, from which a table of corrections may be obtained.

Conversion of Scales.—If it be desired to convert readings on the

Centigrade scale into corresponding Fahrenheit readings, the general relation

$$\frac{\text{C reading}}{5} = \frac{\text{F reading} - 32}{9}$$

may be used. Thus $40^{\circ}\text{C.} = 104^{\circ}\text{F.}$, and $122^{\circ}\text{F.} = 50^{\circ}\text{C.}$ The Réaumur reading divided by 4 is equal to either of the above expressions, but it is seldom necessary, in this country, to take the Réaumur scale into account. It is worthy of notice that any multiple of 5° on the Centigrade scale will correspond to a whole number on the Fahrenheit scale. This arises from the fact that the distances between the fixed points are divided into 100° and 180° respectively, consequently, on the same stem, an interval of 5°C. is equal to 9°F. As the ice-point is marked 0°C. and 32°F. , it follows that $5^{\circ}\text{C.} = (32 + 9) = 41^{\circ}\text{F.}$, and generally $[n\ 5^{\circ}\text{C.} = (32 + n\ 9)^{\circ}\text{F.}]$ This relation is of service in marking both scales on the same stem.

The Fahrenheit scale is still extensively used in this country, both for meteorological and engineering purposes, as well as domestic. It is to be hoped that, for scientific work at any rate, its use will gradually die out, as the use of the arbitrary datum number, 32° , for the ice point, tends to confusion in calculation, and serves no useful purpose. This number was arrived at by the use of a mixture of snow and salt for fixing the lower point, which was called 0° , and the temperature of the human body for the upper point, which was called 96° . A thermometer constructed on this principle showed 32° in melting ice, and 212° in boiling water. Fahrenheit's standards have long been abandoned as untrustworthy, but the cumbersome figures have been retained, presumably as a concession to custom. The fixing of the Réaumur scale was determined by the boiling-point of alcohol which was called 80° , and almost agreed with the Centigrade scale; afterwards steam was substituted for alcohol and the figure 80 retained.

It should be remembered that where an interval of temperature only is considered, 1°C. is the equivalent of 1.8°F. The datum number 32 is only necessary to take into account when actual scale readings are required.

Special Range Thermometers.—When it is required to measure small differences of temperature very accurately, a mercury thermometer covering a range of nearly 400°C. would be unsuitable, as the degrees could not be sub-divided unless the stem were inconveniently long. It is possible, however, to construct thermometers to cover any special range, so as to read fractions of a degree. In such cases

the bulb is made large relatively to the bore, and a safety-space provided to take the mercury should by chance the range be exceeded. For example, a thermometer may be made 15 inches long, with the mark nearest the bulb 0°C. , and the highest mark 30°C. Each degree would then be $\frac{1}{2}$ an inch long, and could be sub-divided into tenths or twentieths. A small bulb is blown at the top into which the mercury will pass if 30°C. be exceeded, without danger of bursting the thermometer. If observations are required over a small range at a higher temperature—say 100° to 130°C. —the lowest mark on the scale is made 100° , and a bulb blown between this mark and the thermometer bulb, which prevents the mercury reaching the scale until a temperature of 100° has been attained. The range is thus restricted, and sub-divided degrees can therefore be obtained on a thermometer of the usual length. In Beckmann's thermometers, by the use of a very large bulb and a narrow-bore tube, the scale is divided into $\frac{1}{100}^{\circ}$. These thermometers are intended to take readings of differences of temperature varying by a few degrees only. The safety-space at the top is bent into a parallel branch with the stem, and any excess of mercury will remain in this space. If, at the lower temperature, the column shrinks into the bulb, it is possible by judicious shaking to cause mercury to pass from the safety-space into the bore, until the end of the column is opposite one of the lower marks on the scale, when the higher reading may be taken. If the column should stand too high on the scale, the bulb is heated so as to drive the excess into the safety-space. These thermometers have come into general use for molecular weight determinations from observations of the depression in freezing point or rise in boiling point of a solvent due to dissolved solids, and for calorimetric observations in which great accuracy is desired.

Registering Thermometers.—There are many methods by which thermometers may be made to register special temperatures, such as the maximum and minimum temperatures experienced during a given time. The simplest form for registering the maximum temperature consists of a mercury thermometer, in the bore of which is placed a glass index, shaped like a dumb-bell. When the mercury rises in the tube the index is pushed forward by the end of the column; and if the thermometer is placed horizontally will remain stationary when the column shrinks owing to cooling. The end of the index next to the column will therefore record the maximum temperature. By attaching a fine steel spring to the index, it may be prevented from falling down the bore by its own weight, and the thermometer may then be kept in a vertical position. When setting for a given obser-

vation the index is shaken down to the top of the column, or, if it possess a steel spring, may be dragged down by a magnet. In another form of maximum thermometer (Fig. 27 A) the bore of the tube near the bulb is made extremely narrow. On heating, the force of expansion is sufficient to drive the mercury through this narrow passage, but on cooling the friction is too great to allow the column in the bore to return to the bulb, and the mercury divides at the constricted part. The end of the column in the bore therefore records the maximum temperature. The mercury in the bore may be made to join on to that in the bulb by jerking the thermometer vertically. This is the principle of the clinical thermometer, which is graduated for the special range of temperature to which the human body is liable.

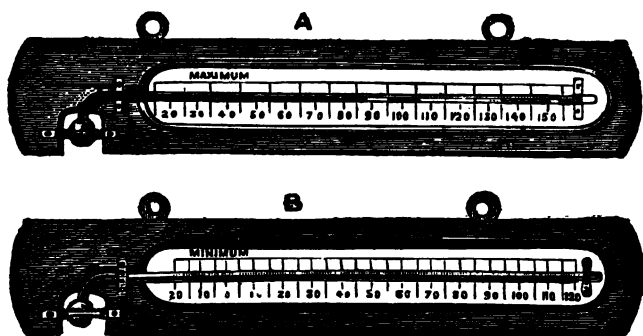


FIG. 27.—MAXIMUM AND MINIMUM THERMOMETERS.

The simplest form of minimum thermometer is made of alcohol, and possesses an index immersed in the liquid in the bore (Fig. 27 B). When the temperature falls, the column of alcohol moves towards the bulb, and the surface skin at the end of the column pushes the index in front of it, the rounded end of the index being unable to penetrate the skin. On the temperature rising, the alcohol expands freely round the index without causing it to move; consequently the end of the index next to the top of the column registers the minimum temperature. The index may be re-set by shaking, or, if it possess a steel spring, by means of a magnet. In Sixe's thermometer (Fig. 28) a maximum and minimum arrangement is provided in the one instrument. The stem of an alcohol thermometer is bent into a U shape, and the column of alcohol interrupted by a thread of mercury, which fills the bend and rises to a suitable height in each

branch of the U-shaped portion. An index is placed at the top of each of the mercury columns. When the temperature rises, the alcohol in the bulb expands, pushing down the mercury in the limb nearest to the bulb, and therefore causing it to rise in the other limb,

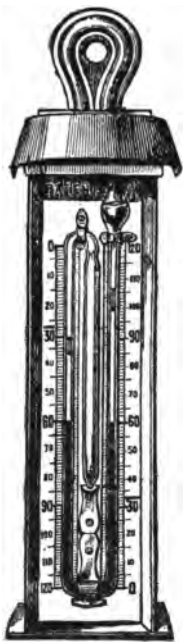


FIG. 28.
SIXE'S MAXIMUM
AND MINIMUM
THERMOMETER.

pushing the index as it rises, and leaving it, sustained by its spring, at the maximum position attained. On cooling, the alcohol shrinks into the bulb, and the mercury in the column nearest the bulb rises, carrying the index in this branch upwards, and leaving it nearer the bulb when the temperature rises. This therefore records the minimum temperature, whilst the other index registers the maximum. Two scales are provided, the graduations being made to represent the position of the top of each mercury column. The scale on the branch nearest the bulb therefore reads downwards, whilst the other scale reads upwards. Sixe's thermometer is very largely used in greenhouses, etc., and is a convenient form of maximum and minimum thermometer.

High Temperature Thermometers.—The upper limit of a mercury thermometer, unless specially made, is the boiling point of the mercury— 357°C . By employing a strong bulb, however, and leaving nitrogen or carbon dioxide gas in the bore, it is possible to obtain higher readings, as the presence of the gas causes pressure to be exerted on the surface of the mercury, and prevents it boiling. By this means it

is possible to construct thermometers reading as high as 500°C ., using a special kind of glass, which, at this temperature, does not undergo permanent distortion even under the high internal pressure. If this temperature be exceeded, however, the glass softens sufficiently to cause a permanent alteration in the size of the bulb, and the readings are then worthless. In Bayly and Chorley's thermometers mercury is replaced by an alloy of sodium and potassium, which boils at over 700°C . Readings beyond this temperature cannot be made with these instruments, as the bulb softens and alters in shape, in spite of the absence of internal pressure. It has recently been proposed to use thermometers made of quartz instead of glass, and, for readings above 250°C ., to employ molten tin as the expanding liquid. A

temperature of 1000°C . might thus be reached without danger of distorting the quartz bulb. These instruments, however, have not yet come into practical use, and for high temperature measurements, instruments based on other principles than the expansion of a liquid must be used.

Gas Thermometers.—The uniformity of the expansion or increase in pressure of the more perfect gases, such as hydrogen or nitrogen, render gas thermometers the most accurate of all instruments for measuring temperature, when properly constructed. Gas thermometers are of two types, viz. (1) constant pressure instruments, in which the gas is allowed to expand at constant pressure, and the temperature deduced from the increase in volume, and (2) constant volume thermometers, in which the gas is prevented from expanding, and the temperature obtained from the observed increase in pressure. Hydrogen is the best gas to use up to 200°C ., owing to the accuracy with which it conforms to the laws relating to a perfect gas; above 200°C ., however, it is liable to attack glass and other materials that might be used. Nitrogen, although less perfect than hydrogen, is free from this objection, and is therefore used when higher temperatures are measured. There are many forms of gas thermometers, and a typical example of each class will now be described.

Callendar's Compensated Constant Pressure Gas Thermometer.—Fig. 29 shows a diagrammatic view of this instrument. T is the thermometer bulb, which is connected to the bulb M, containing mercury, and furnished with a tap. S is a bulb precisely similar to T, and is attached to a tube of the same diameter and length as that connecting T and M. A U-tube, G, containing strong sulphuric acid, connects the two systems of tubes. The bulbs T and S, and also their connections, contain dry hydrogen or nitrogen. In taking a measurement, the bulbs S and M are surrounded by ice, whilst T is placed in the hot space of which the temperature is required. Mercury is now allowed to flow from M until the pressure inside T is equal to that in S, as shown by the sulphuric acid standing at the same level in both limbs of the tube G. Originally, when T, S, and M are all surrounded by ice, the level of the sulphuric acid must also be equal. As the pressure in the tube S is constant, that in the tube T is brought to its original amount when the gauge indicates equality of pressure in the two systems. Any variations in temperature experienced by the tube connecting T and M will be equally shared by the tube connected with S, any possible error from this source being thus compensated. The volume of T being known, the temperature is calculated from the volume of gas which expands into M,

which is equal to the volume of mercury run out to equalise pressures. This volume is obtained by weighing the mercury and dividing by specific gravity. The calculation is made as follows :—

Let V = volume of gas in T , and θ its absolute temperature.

v = volume of gas expanded into M . As M is kept in ice, the absolute temperature of this gas will be 273°C .

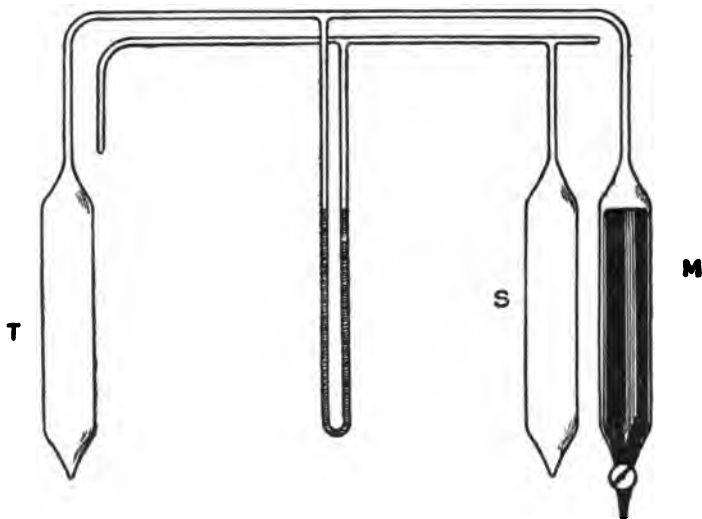


FIG. 29.—CALLENDAR'S COMPENSATED GAS THERMOMETER.

On heating the gas in the bulb to θ , its volume will become, by Charles' Law, $\frac{V \theta}{273}$, the pressure being constant. The expanded portion, at the same temperature, would have a volume equal to $\frac{V \theta}{273} - V$. But in passing into the bulb M its temperature is reduced to that of ice, or 273°C . absolute. Hence the volume of expanded air collected in M , which is equal to v , will be

$$\left(\frac{V \theta}{273} - V \right) \times \frac{273}{\theta} = v$$

$$\therefore \frac{V \theta - 273 V}{\theta} = v$$

$$\text{and } \theta = \frac{273 V}{V - v}$$

The result is given in absolute degrees, and it is assumed that the gas strictly obeys the gaseous laws, and that the compensation is perfect. When used for low temperatures, with hydrogen, the deviation from the gaseous laws may be ignored; with nitrogen, on the contrary, a slight correction must be made on this account. The error in using this instrument to measure a temperature as high as 450°C . probably does not exceed 0.2° , and although the arrangement is too elaborate for everyday use, it is of great value for standardising instruments of a more convenient type. It is the most accurate form of constant pressure gas thermometer, and if furnished with a quartz or platinum bulb may be used for temperatures exceeding 1000°C . This instrument has proved useful in furnishing standards for the graduation of pyrometers.

Example.—If the volume of gas in the bulb when in ice is 75 c.c., and on heating, 40.9 c.c. pass over into the mercury tube when the pressures are equal, the temperature will be

$$\frac{273 \times 75}{75 - 40.9} = 600.4^{\circ} \text{ absolute,}$$

$$\text{or } (600.4 - 273) = 327.4^{\circ}\text{C}.$$

For many determinations dry air, free from CO_2 , may be used with sufficient accuracy.

Jolly's Constant Volume Gas Thermometer.—The constant volume gas thermometer selected for description is one of many varieties, and possesses the advantages of simplicity and considerable accuracy. In Fig. 30 B is the thermometer bulb, connected by means of narrow-bore tubing to the rubber tubing, T, which at the other end communicates with a mercury cistern. The cistern may be raised or lowered along the guide G, and clamped in any position. A scale is attached to the stand and enables the height to which the mercury has been raised to be read off. A mark is engraved on the tube A, at which the mercury is retained by raising the cistern when the temperature of the bulb rises, or lowering when the temperature falls, thus keeping the volume of enclosed gas constant. To use the instrument with air, the mercury cistern is lowered below the mark on A, and the tap C, connected with a drying tube containing calcium chloride, is opened. The bulb is now placed in powdered ice, and allowed to remain for some time in order that the temperature of the enclosed air may fall to 0°C . The cistern is then raised until the mercury rises to the mark on A, when the tap is closed and the height of the surface of the mercury in the cistern read off on the

scale. The bulb is now placed in the space of which the temperature is required, and the cistern adjusted so as to retain the mercury at the mark on A. When steady, the height of the mercury surface in the cistern is again read, and the temperature deduced as under :--

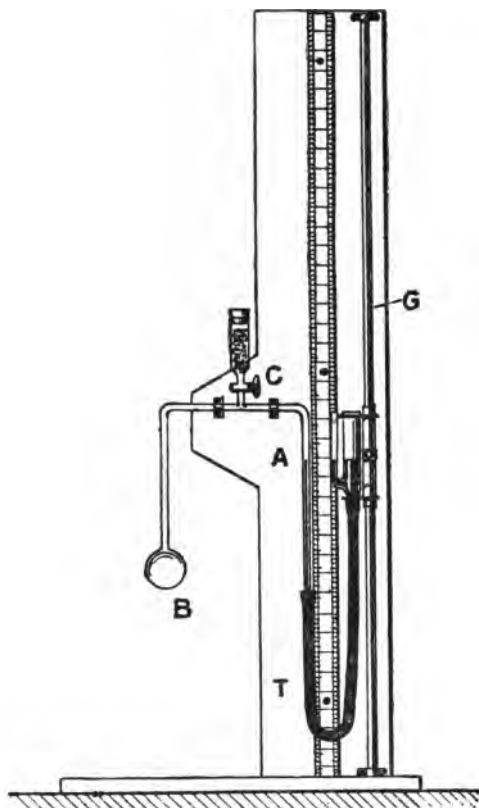


FIG. 30.—CONSTANT VOLUME AIR THERMOMETER.

If the gas used be considered perfect, the relation

$$\frac{PV}{T} = \frac{P_1 V_1}{T_1}$$

may be applied at all temperatures and pressures. If the slight expansion of the bulb be neglected, $V = V_1$, therefore

$$\frac{P}{T} = \frac{P_1}{T_1}.$$

In the experiment, by opening the tap, P = barometric pressure, and T = temperature of melting ice = 273° abs. If h = the *difference* in level of the mercury in the cistern when the bulb is in ice and the hot space respectively, P_1 = barometer height + h .

Hence

$$\frac{\text{Baro.}}{273} = \frac{\text{Baro.} + h}{T_1},$$

$$\therefore T_1 = \frac{(\text{Baro.} + h) \times 273}{\text{Baro.}}$$

When hydrogen gas is used, the above calculation gives an almost perfectly correct result for temperatures below 200° C., provided due allowance be made for certain incidental errors. A correction is necessary for (a) the expansion of the bulb, which cannot be avoided, hence V is not exactly equal to V_1 ; (b) the temperature of the gas in the narrow-bore connecting tube, which is not equal to that in the bulb; and (c) the temperature of the mercury column, which, as in the case of the barometer, should be reduced to the equivalent reading at 0° C. Owing to the large mass of gas used, the combined errors are relatively small, but must be taken into account if standard readings are required. If the temperature be less than that of ice, the pressure must be diminished by lowering the cistern, in order to maintain constant volume, in which case the difference of level (h , will be negative.

Examples.—(1) If the increase of pressure be 241 mm., and the barometer reading 755 mm., the temperature will be

$$\frac{(755 + 241) \times 273}{755} = 360.2 \text{ abs.},$$

$$\text{or } (360.2 - 273) = 87.2^{\circ} \text{ C.}$$

(2) When used to take a low temperature, the mercury in the cistern was lowered 310 mm. below the starting point to maintain constant volume. Height of barometer = 762 mm. Hence the temperature was

$$\frac{(762 - 310) \times 273}{762} = 161.9^{\circ} \text{ abs.}$$

$$\text{or } (161.9 - 273) = -111.1^{\circ} \text{ C.}$$

If nitrogen or air be used in the thermometer, the calculation must be modified, as the increase of pressure at constant volume differs sensibly from $\frac{1}{273}$, which almost exactly represents the coefficient for hydrogen. Nitrogen is the best gas to employ for general work, being inert towards the material of the bulb at all temperatures. The coefficient of increase of pressure at constant volume for nitrogen is not constant, being greater at 0° than at 100° , the respective values being $\cdot 003677$ and $\cdot 0036738$, or $\frac{1}{271\cdot 9}$ and $\frac{1}{272\cdot 1}$ when the original pressure is 1 metre. Careful investigations of the value of the coefficient at different temperatures have been made, thus enabling correct calculations to be made. In the previous examples, if nitrogen were used, the reciprocal of the coefficient known to apply to the range of temperature measured must be used instead of the figure 273. Thus in example (1), if the same figures had been obtained with a nitrogen thermometer, the temperature would be

$$\frac{(755 + 241) \times 272}{755} = 358\cdot 9^\circ \text{ abs.} = 85\cdot 9^\circ \text{ C.}$$

since the coefficient has an average value of $\frac{1}{272}$ over this range. By correcting for the incidental errors previously mentioned, and using the proper coefficients, very exact results may be obtained with the constant volume nitrogen thermometer, which represents one of the best standards for temperature measurement. For rougher determinations, in which air is used, close results may be obtained in the manner described, using the figure 272·5 instead of 273 in the calculation. In the standard instruments used at Sèvres, the National Physical Laboratory, and elsewhere, various refinements are embodied which enable very exact readings to be obtained.

The constant volume hydrogen thermometer is specially suited to the measurement of very low temperatures, such as those of liquid or solid air. Under the reduced pressure, the gas approaches closely in properties to a perfect gas, and accurate readings are obtained. For the temperatures of liquid or solid hydrogen ($-252\cdot 5$ and -257° C.), helium may be used in the thermometer, although good results may be obtained even with hydrogen, as the enclosed gas, being under a very low pressure, shows no tendency to liquefy, and continues closely to obey the gaseous laws. Professor Dewar has conducted his low temperature measurements in this manner, and the values obtained are very near to the truth. If absolute zero were

reached, the mercury in the cistern would have to be lowered by an amount equal to the initial pressure, in which case

$$\frac{P}{T} = \frac{P_1}{T_1} \quad \text{or} \quad \frac{\text{Baro.}}{273} = \frac{(\text{Baro.} - h)}{T_1} = \frac{0}{T_1}$$

∴

$$T_1 = 0^\circ \text{ abs.}$$

The physical meaning of this is that the gas would cease to exert pressure, and in this respect behave like a vacuum.

For high temperatures, the bulb of the instrument may be made of quartz, platinum, or an alloy of platinum and iridium; nitrogen gas being employed, as hot hydrogen slightly attacks quartz, and is occluded by platinum. It has been found possible by this means to measure temperatures correctly up to 1150° C. , and so to establish standards for the graduation of the instruments described in the succeeding chapter.

The most recent development of the gas thermometer is due to Day, who has employed a bulb made of platinum, 80 per cent., and rhodium, 20 per cent., surrounded by an outer vessel. The space between the bulb and its enclosure was kept at the same pressure as that existing in the bulb, distortion being thus prevented. It was found possible to take accurate readings up to 1550° C. , the error not exceeding $\pm 2^\circ \text{ C.}$ This extension of the gas scale has already proved of considerable service in checking the readings of other instruments used in the measurement of high temperatures.

CHAPTER VIII.

THE MEASUREMENT OF HIGH TEMPERATURES. PYROMETRY.

THE term "pyrometry" is used to embrace all the methods of measuring temperatures above the upper limit of liquid-in-bulb thermometers. With mercury, the limit is 500°C. , the thermometer containing nitrogen under pressure; and with sodium-potassium alloy 700°C. may be measured with fair accuracy. If we except the proposed tin-in-quartz thermometer, not yet in practical use, all temperatures above 700°C. must be determined by other methods. None of these methods, however, can compare in cheapness and ease of reading with the ordinary thermometer, which is consequently used wherever possible.

The importance of conducting furnace operations at definite, known temperatures is now fully realised by manufacturers. In the manufacture and subsequent treatment of steel, for example, the temperature at which the operation is carried out has a determining influence on the finished product, which likewise holds true in the casting of alloys, the baking and glazing of pottery, and many other industrial operations. The recognition of these facts has led to the introduction of numerous forms of pyrometers for industrial purposes, and almost every establishment of consequence has now its installation of pyrometers. Great advances have been made in recent years in the accurate measurement of high temperatures, and it is now possible to read the temperature of a furnace with a degree of accuracy equal to the reading of a low temperature with an ordinary mercury thermometer. It will probably be possible, before many years, to measure with reasonable certainty temperatures of over 3000°C. , such as that of the electric arc. So numerous are the modern developments of pyrometry, that a special volume would be required for a complete treatment of the subject, and it is only proposed in the present chapter to give a description of the more typical pyrometers in use at the present time, and to indicate their practical utility. It may be taken for granted that any workshop pyrometer should, as far as possible, give an automatic registration of the temperature, in order

that workmen who have had no scientific training may be able to take the necessary readings.

The methods in use for obtaining furnace temperatures may be summarised as follows :—

1. Wedgwood's Pyrometer, based on the permanent contraction of a clay cylinder when heated. The amount of contraction observed gives a clue to the furnace temperature.

2. Calorimetric method, in which a weighed piece of metal is taken from the furnace and dropped into water, the temperature being obtained from the rise in temperature of the water.

3. Gas Pyrometers, which are based on the increase in volume or pressure of a gas.

4. Electrical-resistance Pyrometers, which depend on the increase in resistance to electricity shown by platinum as the temperature rises.

5. Thermo-electric Pyrometers, which utilise the electromotive force developed at a junction of two different metals. With suitable metals, the E.M.F. increases in a regular manner as the temperature rises.

6. Heat-Radiation Pyrometers. In these instruments the temperature is deduced from the heat radiated by a given surface, which is a function of the absolute temperature of the surface.

7. Optical Pyrometers, based on a comparison of tints, or a photometric measurement of a given part of the spectrum.

8. Pyrometers based on the linear expansion of a metal, the temperature being deduced from the observed elongation.

9. Fusion method, which consists in the insertion in the furnace of a graded series of materials with known melting points, the temperature being approximately that of the highest member of the series which has undergone fusion.

It may be stated that methods 4, 5 and 6 are the most useful in practice, and possess the advantage of being capable of giving automatic and continuous records of the temperature of a furnace.

Fixed Points for Graduation of Pyrometers.—In order that pyrometers of different types may read alike, it is necessary to graduate them in terms of a common, accurate scale of temperature, for which purpose the gas scale is adopted. A series of fixed points, accurately determined by means of a gas pyrometer or by other methods, serve as standards of temperature for the graduation of the various forms of pyrometers, and uniformity is thus secured. Within very narrow limits, the table of fixed points given below may be considered as correct up to 1150°C. , above which it has not yet been found pos-

sible to apply the gas pyrometer method. The melting point of platinum is still uncertain, a recent determination by Dr. Harker, viz. 1710°C ., being 70 degrees lower than the previously accepted figure; whilst the still later determination by Burgess is 1753°C . Above 1150°C . the values are obtained by assuming that the indications of a thermal-couple pyrometer follow the same law as that known to exist below this temperature, or by calorimetric, optical, or radiation methods; consequently the accuracy of these higher temperatures cannot be definitely asserted. The following table gives the most accurate results obtained up to the present:—

TABLE OF FIXED POINTS.

	Temp. in deg. C.
Boiling point of water, at 760 mm. press.	100
„ naphthalene „	220
Freezing point of pure tin	232
„ „ lead	327
„ „ zinc	419
Boiling point of sulphur at 760 mm. press.	444.6
Freezing point of pure antimony	632
„ „ silver (in absence of oxygen)	962
„ „ gold	1065
„ „ copper (covered with graphite)	1084
„ „ wrought iron	1510
„ „ platinum (formerly called 1780)	1710 (Harker)
„ „ „ „	1753 (Burgess)
„ „ iridium	2250 (?)

When standardising a pyrometer by means of the above fixed points, special precautions are necessary with copper and silver. If exposed to air, silver occludes oxygen, and the freezing point is lowered. The observation should therefore be taken in an atmosphere of nitrogen, the silver being melted in a graphite crucible. Melted copper oxidises in air, forming an oxide which mixes with the metal and reduces the freezing point to 1062° . If the copper be melted in a graphite crucible and covered with graphite the freezing point is 1084° ; if freely exposed to air the figure 1062° may be taken, as the effect of oxidation reaches a permanent limit, and a steady freezing point is then obtained at the lower temperature. It is not necessary to employ every fixed point in standardising a pyrometer for ordinary use, the following usually sufficing:—steam, tin, zinc, antimony, silver and copper. Higher points may be obtained by extrapolation when required, and a good, cheap substitute for silver is furnished by pure anhydrous sodium sulphate, which freezes at 900°C . approximately. Pure common salt freezes at 800°C . (approx.)

Where a number of pyrometers are used, it suffices to standardise one instrument exactly, which may then serve to graduate the others by comparison, and be kept as a standard for checking the remainder from time to time.

The various types of pyrometer will now be described in the order in which they occur in the summary previously given.

1. *Wedgwood's Pyrometer.*—Wedgwood, the potter, was the first to recognise the value of working at uniform temperatures in his furnaces, so as to avoid uncertainty in results. He found that mere judgment by the eye could not be relied upon, and in the year 1782 constructed a pyrometer for his own use, which has only been superseded by the more scientific instruments produced during the last thirty years, and is still used to some extent. Wedgwood found that clay, of definite composition, undergoes a permanent contraction on

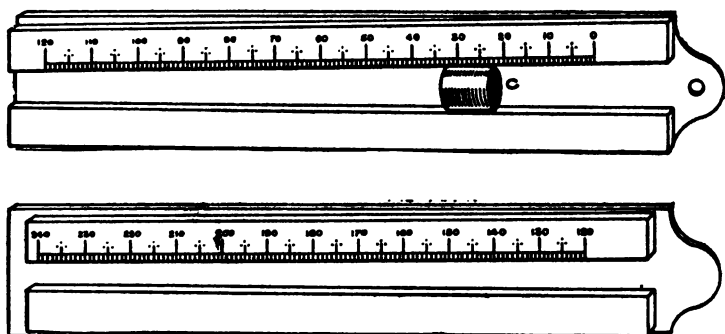


FIG. 31.—WEDGWOOD'S PYROMETER.

heating, and the higher the temperature the greater the amount of permanent contraction. To establish a standard of reference, he made a tapering groove, divided along its length, as shown in Fig. 31. The clay cylinder C, is made of such a size that before placing in the furnace it slides into the groove down to the mark "o." After remaining in the furnace long enough to acquire the existing temperature, the clay cylinder is removed and allowed to cool, and again placed in the groove. The mark opposite the lower end of the cylinder then records the condition of the furnace in terms of the scale adopted by Wedgwood, and any considerable variation on either side of the desired temperature is thus readily detected. Although this method cannot compare for accuracy or convenience with modern pyrometers, it is nevertheless a useful guide to the state

of a furnace, and is further of interest as being the first attempt at obtaining precision in work at high temperatures. Wedgwood's divisions or degrees were taken in terms of $\frac{1}{2400}$ of the initial dimensions so that at 240 divisions the diameter was reduced by one half. The connection between these divisions and Centigrade degrees has been investigated by Le Chatelier, who gives the following figures:

Degrees Wedgwood	15	30	100	140
Degrees Centigrade	800	1000	1200	1400

Wedgwood's pyrometer, on account of its cheapness, is still used to some extent by potters and others.

2. *Calorimetric Method of Obtaining Furnace Temperatures.*—If a weighed piece of metal, of known specific heat, be made hot, and immersed in a known quantity of water, the temperature of the hot metal can be inferred from the rise of temperature produced in the water.

Example.—A copper cylinder weighing 140 grams is heated in a furnace, and rapidly immersed in 550 grams of water at 18.7°C . The water is contained in a copper vessel weighing 250 grams, and the final temperature is 30.2°C . The specific heat of copper is 0.095. Find the temperature of the furnace.

Let x = temperature of furnace.

Heat units lost by hot copper = heat units gained by water and vessel

$$140 \times 0.095 \times (x - 30.2) = 550 \times (30.2 - 18.7) + \{250 \times 0.095 \times (30.2 - 18.7)\}$$

$$\therefore x = 526.3^{\circ}\text{C}.$$

In attempting to construct an instrument based on this principle, several difficulties arise. If the piece of metal is to be used continuously, it should not oxidise, or its weight would alter. Platinum, in this respect, would be most suitable, but the cost of a piece of sufficient size would be greater than that of a good pyrometer of another type. Nickel is the only metal which can be used with advantage for this purpose. Again, the specific heat of a metal varies with the temperature, and this must be taken into account in the calculation. It is also difficult to prevent loss of heat by radiation in transferring the metal from the furnace to the water, and in its best form a workshop pyrometer on this principle cannot be trusted to

25° C. In Siemens' instrument, Fig. 32, the vessel containing the water is well insulated with felt, and the outer vessel furnished with a handle for convenience of holding near the furnace. A scale C, is attached, graduated in such a manner that if the zero mark be placed opposite the top of the mercury column in the thermometer before starting, the temperature of the hot metal may be read off opposite the top of the mercury at the end of the experiment. Calculations are thus avoided, and the instrument may be used by an untrained observer. Copper cylinders are sometimes used with this apparatus, but are subject to loss of weight owing to oxide forming and afterwards peeling off. Multiplying factors are sent out with the instrument, which enable the error due to loss of weight to be allowed for. It is preferable, however, to use nickel, which oxidises very little below 1000° C.

Whilst the calorimetric method is cheap and fairly accurate if carefully used, it suffers from the drawback that a continuous reading cannot be obtained, and a separate experiment must be performed whenever the temperature is required. Experience shows that a skilled observer is essential if good results are to be obtained, as in the hands of workmen errors arise through delay in dropping the hot metal into the water, or through neglect of other necessary precautions. This form of pyrometer is fairly extensively used, on account of its cheapness, for operations in which an occasional reading of the temperature suffices.

3. *Gas Pyrometers.* The principle of these instruments has been sufficiently indicated in the previous chapter. Although furnishing a standard of temperature with which other pyrometers are compared, gas pyrometers are too elaborate, and require too delicate manipulation to enable them to be used in industrial operations. The extensive researches of Holborn and Day at the Reichsanstalt with a constant volume nitrogen thermometer have resulted in the satisfactory settlement of fixed points up to 1100° C., which may be used in graduating other instruments. These observers first of all used a porcelain bulb, glazed inside and out; but after-

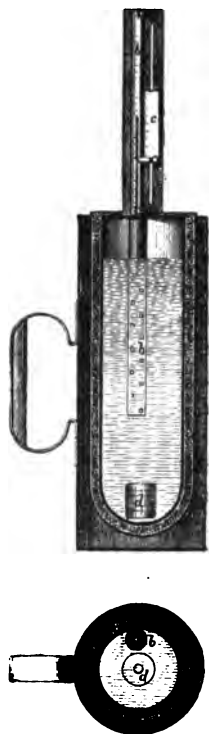


FIG. 32.—SIEMENS' CALORIMETRIC PYROMETER.

wards found that a bulb made of platinum-iridium alloy is more satisfactory, as the latter is not only impervious to nitrogen, but undergoes no permanent alteration in shape on heating. More recently, Jacquerod and Perrot have used a quartz bulb, which, owing to the low coefficient of expansion of quartz, reduces the necessary correction for expansion to a minimum. With a platinum-iridium bulb the expansion correction at 1000°C. is 40° ; with quartz at the same temperature the correction is only 2° . It is advisable, in a standard constant volume instrument, to employ a bulb of at least 500 c.c. capacity, in order that the error due to unheated gas in the connections may be less than 1° .

In Wiborgh's air pyrometer an attempt is made to read temperatures from the indications of a Bourdon pressure gauge. A definite quantity of air is forced into a porcelain bulb placed in the furnace by causing a lens-shaped chamber to collapse and discharge its contents into the bulb. The bulb communicates with a pressure gauge, and the positions of the index hand of the gauge are made to indicate corresponding temperatures. This instrument must not be regarded as possessing the accuracy of a standard gas pyrometer, as the calibration is purely empirical. There is also a danger of leakage at the junction of the porcelain bulb and the gauge tube.

4. *Electrical Resistance Pyrometer.*—When platinum is heated, its resistance to electricity increases rapidly with the temperature. Thus a piece of pure platinum wire, having a resistance of 2.6 ohms at 0°C. , increases its resistance to 3.6 ohms at 100°C. , that is, gains 1 ohm for a rise of 100° . If this increase be considered uniform between 0° and 100° , then each increment of $\frac{1}{100}$ of an ohm resistance would indicate a rise of 1° . As it is easily possible to measure $\frac{1}{1000}$ of an ohm, it follows that on the above assumption $\frac{1}{10}$ of a degree could be indicated by noticing the increased resistance of the piece of wire.

Sir William Siemens was the first to propose, in 1871, the utilisation of the increase in resistance of platinum for the measurement of furnace temperatures; and constructed pyrometers consisting of a piece of fine platinum wire wound on a porcelain or fire-clay cylinder incased in a steel tube to protect the platinum from the action of the furnace gases. The resistance was measured by a set of coils and galvanometer, and the temperature deduced from the resistance by means of a formula connecting the readings with temperatures on the air scale. As constructed, the instrument was found to be unreliable, owing to the resistance of the platinum undergoing a permanent increase after heating, as the result of a chemical change due in part

to the porcelain, and partly also to the furnace gases, which to some extent penetrated the iron tube. Later this trouble was overcome by the use of magnesia, in which the platinum wire, wound on a special kind of fire-clay, was imbedded, a procedure still adopted in Siemens' pyrometers as now sold.

In 1886, Professor Callendar investigated the subject, and showed that the method was capable of giving very accurate results under proper conditions. Callendar wound the wire round mica, and encased the arrangement in a glazed porcelain tube, and then found that repeated heatings caused no appreciable alteration in the metal.

The question of the connection between the increase of resistance and gas thermometer temperatures was investigated by Callendar and Griffiths up to 550°C. , and formulæ deduced from which gas scale readings could be obtained to within 0.1° by the use of a properly wound platinum wire. The formulæ are as follows:—

1. Let R_0 = resistance in melting ice
 R_{100} = resistance in steam at 760 mm.

Also let $R_{100} - R_0$ be assumed to equal 100° on the platinum scale, then 1 degree will be equal to $\frac{R_{100} - R_0}{100}$. Assuming that an increase of resistance of this amount represents 1 degree at all parts of the scale, then if R be the resistance observed in a given space, the temperature, in terms of the platinum scale, will be

$$\frac{\text{increase of resistance observed}}{\text{increase of resistance for } 1^{\circ}}$$

or,

$$\frac{R - R_0}{R_{100} - R_0} = \frac{R - R_0}{R_{100} - R_0} \times 100.$$

Example.—If the resistance in ice be 2.6 ohms, in steam 3.6 ohms, and in a furnace 12.8 ohms, the temperature of the furnace, on the platinum scale, will be

$$\frac{12.8 - 2.6}{3.6 - 2.6} \times 100 = 1020^{\circ} (\text{Pt})$$

2. An increase of resistance at any part of the scale equal to $\frac{R_{100} - R_0}{100}$ does not correspond exactly to 1 degree on the gas scale.

The connection between the two scales is expressed in the equation:—

$$t - P t = \delta \left\{ \left(\frac{t}{100} \right)^2 - \left(\frac{P t}{100} \right)^2 \right\}$$

where t = temperature on the air thermometer

$P t$ = temperature in terms of platinum scale

δ = a constant, depending on the purity of the platinum.

This constant must be determined experimentally, and in order to obtain the value, $P t$ must be determined at some temperature other than 0°C. and 100°C. , at which, by definition, it coincides with the air scale. The temperature usually selected is the boiling point of sulphur, which Callendar found to be 444.5°C. on the air scale, at a pressure of 760 mm. A difference of ± 1 mm. alters the boiling point of sulphur $\pm 0.082^\circ \text{C.}$ The platinum temperature of boiling sulphur is found by measuring the resistance at 0° (ice), 100° (steam) and in the boiling sulphur, and calculating as in the previous example. A further example will make the procedure clear, and show how δ is determined from the data.

Example.—The resistance of the pyrometer in ice is 2.6 ohms, in steam 3.6 ohms, in boiling sulphur 6.815 ohms. Required the value of δ .

The platinum scale temperature of the sulphur will be

$$\frac{6.815 - 2.6}{3.6 - 2.6} \times 100 \text{ (see previous example)}$$

$$= 421.5^\circ (P t)$$

Applying in the formula $t - P t = \delta \left\{ \left(\frac{t}{100} \right)^2 - \left(\frac{P t}{100} \right)^2 \right\},$

$$t = \text{air scale temperature} = 444.5$$

$$\therefore 444.5 - 421.5 = \delta \left\{ \left(\frac{444.5}{100} \right)^2 - \left(\frac{421.5}{100} \right)^2 \right\}$$

$$\text{from which } \delta = 1.5.$$

The value of δ for pure platinum is as nearly as possible 1.5, but should be determined for each batch of wire made into pyrometers by the makers, and sent out with the instrument.

When the value of δ has thus been determined, air-scale temperatures corresponding to given platinum-scale temperatures may be calculated from the equation. A table is appended showing corresponding temperatures as indicated by the two scales, and also the difference between them, when the value of δ is 1.5.

Comparison of Air and Platinum Scales.

$$\delta = 1.5.$$

Platinum Thermometer Reading (Pt.)	Air Thermometer Reading t (deg. C.)	Difference ($t - \text{Pt.}$)
- 100	- 97.1	+ 2.9
0	0	0
50	49.6	- .04
100	100	0
200	203.1	3.1
300	309.8	9.8
400	420.2	20.2
500	534.9	34.9
600	654.4	54.4
700	779.4	79.4
800	910.7	110.7
900	1049.4	149.4
1000	1197.0	197.0
1100	1355.0	255.0
1200	1526.7	326.7
1300	1716.0	416.0

From these values a curve may be plotted, by means of which the figure to be added to the platinum scale to convert into air-scale readings may be deduced for any temperature. Fig. 33 shows such a curve, in which the ordinates represent correction numbers ($t - P$), and abscissæ values of P to which the correction is applied.

The result of the researches of Callendar and Griffiths has been to establish the use of the platinum resistance method for temperatures between -200°C. and $+1000^{\circ}\text{C.}$, when great accuracy is required. When the readings are reduced to the air scale, as shown, the difference between this corrected result and an actual determination by the gas thermometer is extremely small, and the platinum thermometer is much simpler to use. Consequently between these ranges the plati-

L

num instrument is the best practical appliance for accurate working. Its chief drawbacks, as will be pointed out later, are the fragile character of the porcelain shield and alteration in resistance with continuous use. Certain terms connected with the constants of

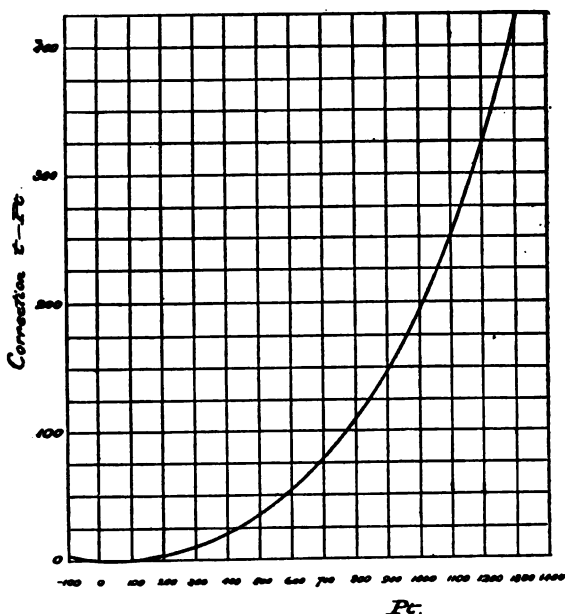


FIG. 33.—CURVE FOR CONVERSION OF PLATINUM-SCALE INTO AIR-SCALE TEMPERATURES.

platinum resistance thermometers have come into use and will now be defined :—

1. *The Fundamental Interval* is the increase of resistance between 0° C. and 100° C., or $R_{100} - R_0$.
2. *The Fundamental Coefficient* is that fraction of the resistance at 0° C. by which it increases per degree between 0° C. and 100° C., or,

$$\frac{R_{100} - R_0}{R_0 \times 100}$$

3. *The Fundamental Zero* is the temperature, in platinum scale degrees, at which the resistance would become zero. It is evidently the reciprocal of (2) prefaced by a minus sign

or,

$$= \frac{R_0 \times 100}{R_{100} - R_0}$$

4. *The Difference Formula* is the expression which shows the relation between air-scale and platinum temperatures,

or,

$$t - P t = \delta \left\{ \left(\frac{t}{100} \right)^2 - \left(\frac{t}{100} \right) \right\}$$

5. *The Platinum Constant* is δ in the above expression.

The method of measuring the electrical resistance will now be explained, and the practical forms of the instrument described.

Measurement of Electrical Resistance of Pyrometer Wire.—The Wheatstone Bridge method of measuring resistance is generally adopted, although in some forms the differential galvanometer method

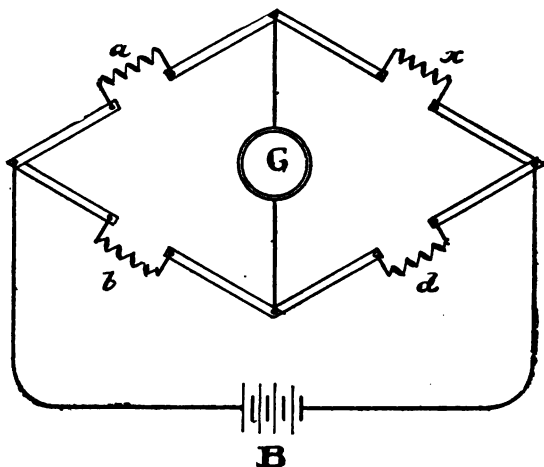


FIG. 34.—PRINCIPLE OF WHEATSTONE BRIDGE.

is employed. The usual quadrilateral representing the principle of the Wheatstone Bridge method is shown in Fig. 34, where a and b are fixed, known resistances, d an adjustable resistance, and x the unknown. When d is so adjusted that on sending a current through the system no deflection is obtained on the galvanometer, then $\frac{a}{b} = \frac{x}{d}$ or $x = \frac{a \times d}{b}$. This principle is applied to the measurement of the pyrometer wire as shown in Fig. 35. The pyrometer is placed in the branch x , and a compensating lead (the use of which will be

explained in describing the pyrometer) in the arm d , in addition to the usual coils, which are adjusted until no deflection is observed, and the resistance deduced from the ratio given above, a being made equal to b . A modified form of bridge is used for very precise measurements; good results may also be obtained with an accurate Post Office box of resistances.

In the differential galvanometer method, which is less sensitive than the foregoing, a current of electricity is made to divide itself between the pyrometer wire and an adjustable resistance, the separate branches of the current passing round the coils of a differential galvanometer, so that the tendencies to deflect the needle are opposed.

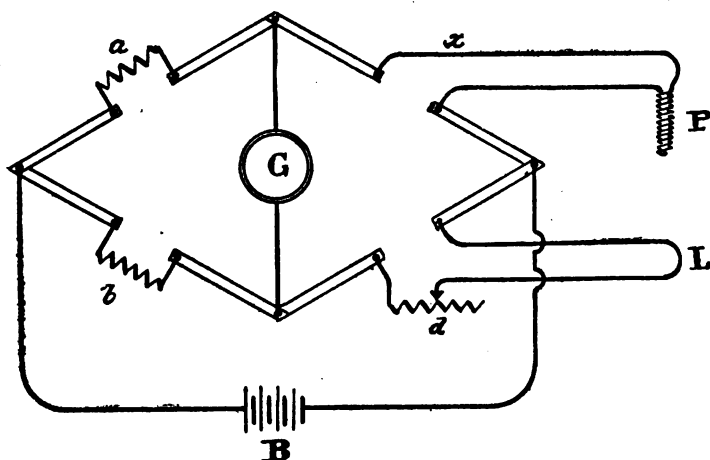


FIG. 35.—WHEATSTONE BRIDGE, AS USED FOR MEASURING THE RESISTANCE OF A PYROMETER.

When the needle is not deflected, the current—and consequently the resistance—in the two branches is equal. The resistance indicated by the adjustable branch of the circuit, when no deflection is observed, is therefore also that of the pyrometer.

Construction of Platinum Resistance Pyrometers.—The Callendar and Griffiths instrument, as constructed by the Cambridge Scientific Instrument Company, is illustrated in Fig. 36. The lower end consists of two strips of mica fastened along their length at right angles to one another, so as to form a + in section. A thin platinum wire is wound in the form of a double thread, round the edges of the mica strips, the ends being connected to leads which are threaded through mica disks and which pass to the terminals at the head of the instru-

ment. A pair of dummy leads, similar in every respect to the ordinary leads, are also threaded through the mica disks, and pass to two other terminals in the head. These dummy leads are joined together at the lower end; and the whole arrangement is encased in a porcelain tube, which fits at the top into a wooden head which serves as a handle. The thin wire is double-wound to prevent the effects of induction when a current of electricity passes in the process of measuring its resistance, and the + shape of the mica round which it is wound reduces the area of contact between metal and mica to a minimum. The mica disks prevent contact between the leads and the porcelain cover, and give stability to the whole arrangement. When the pyrometer is placed in a furnace, it is only necessary to insert it to a sufficient extent to enable the thin wire to acquire the temperature, as, although the leads will alter in temperature and resistance, the dummy leads, being opposed to them in the measuring arrangement, exactly counter-balance any changes in resistance which may occur in the main leads. Hence the actual resistance measured is that of the thin wire, which, at 0°C. , ranges in different instruments from 2.5 ohms to 10 ohms, the latter figure being the normal resistance of a modern Siemens' pyrometer.

Temperature Indicators.— Obviously a workman could not be expected to manipulate a refined form of Wheatstone Bridge, and make the necessary calculations, apart from which such an operation would involve a considerable time. Accordingly, for workshop and general use, indicators have been devised which give a temperature reading directly. In the earliest form of Siemens' pyrometer, the resistance was measured by a differential galvanometer and box of coils, and the temperature corresponding to the resistance, obtained by reference to a table furnished with the instrument. A certain number of these are still in use, but are gradually being supplanted by more modern forms of indicator.

The pattern now sold by Siemens and Co. is illustrated in Fig. 37.

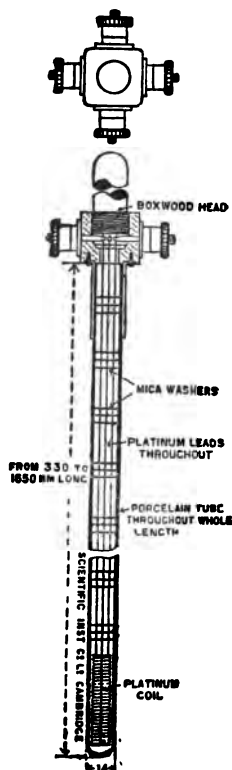


FIG. 36.—PLATINUM RESISTANCE PYROMETER.

It is so arranged that when the lettered terminals of the pyrometer tube are connected to the corresponding terminals of the indicator, and a battery also connected, a Wheatstone Bridge arrangement is formed. The adjustable resistance consists of a wire, wound spirally



FIG. 37.—SIEMENS' INDICATOR FOR PLATINUM RESISTANCE PYROMETER.

round a core, and bent into a circle round the outer side of the instrument. Contact with this wire is made by means of a key, which is fastened by an arm to the centre of the indicator, and may be revolved round the circumference, so as to oppose a greater or less length of wire to the resistance of the pyrometer. A sensitive galvanometer is placed on the top of the indicator, and the key is moved and depressed until no movement of the galvanometer needle is observed. The dial, instead of recording resistance, is made, by calculation, to indicate the corresponding temperature. This arrangement is simple and accurate, and requires no skill to use, all calculations being obviated.

In the earlier form of indicator made by the Cambridge Scientific Instrument Company, a switch moving over a series of studs with which it makes contact, introduces a resistance in opposition to the pyrometer. The progressive resistance between the studs corresponds to 100°C. , so that if the galvanometer indicated 600° as too little, and 700° as too much, the temperature would lie between these limits.

By turning a milled head on the top of the indicator, a scale, divided into 100 equal parts, is rotated, the operation adding a gradually increasing resistance to that already introduced by the switch. Each division on the scale represents 1° , and it is so arranged that the galvanometer needle, when at rest, lies over the number to be added to the reading marked on the plug with which the switch is in contact. Thus if the switch be on plug "600," and "84" on the scale opposite the galvanometer needle when at rest, the temperature is 684° . Many of these are in use, and give very good results, but are not so simple in use as the Siemens' indicator.

The latest form of indicator issued by the Cambridge Scientific Instrument Company is named after the designer, Mr. Whipple. Fig. 38 illustrates the Whipple indicator, which is compact, simple to

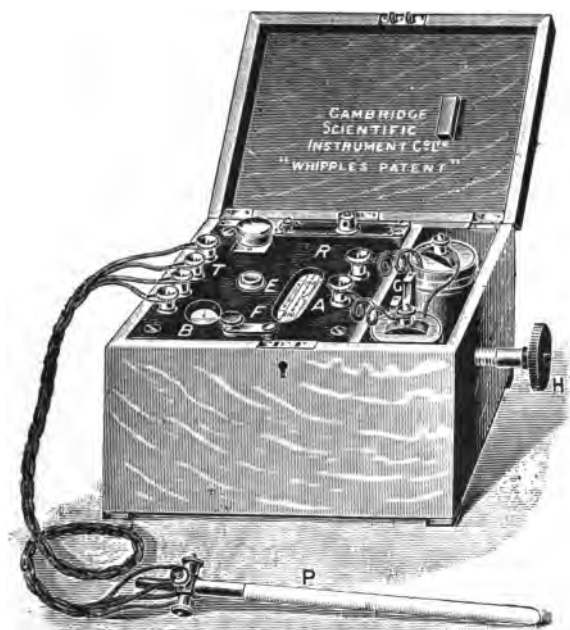


FIG. 38.—WHIPPLE'S INDICATOR.

use, and capable of being read to less than 1° to temperatures above 1000° C. The resistance opposed to the wire of the pyrometer is wound round a drum, to the axis of which a screw, working in a nut, is attached. By turning a handle at the side of the instrument the

drum is rotated, and also, owing to the screw, moved backwards or forwards by the same motion. This operation varies the resistance opposed to the pyrometer, and is continued until, on pressing a key, the galvanometer needle is at rest. The drum is surrounded by a paper, on which a spiral line is drawn, divided into degrees, and the arrangement is such that the number opposite a pointer fixed in the top of the apparatus, and viewed through a narrow window, represents the temperature of the pyrometer. This indicator is as simple to use as the Siemens instrument, and gives an exact reading. By placing the battery in the box containing the rest of the apparatus, portability is secured, everything being ready to take a reading as soon as the pyrometer is coupled up. It may be pointed out that the readings of any indicator, are only correct for the pyrometer with which it is intended to be used, and if the pyrometer should alter in resistance, the readings will be erroneous.

Recording Apparatus for Platinum Resistance Pyrometers.—It is often desirable to obtain a continuous record of the temperature of a furnace or other place, so as to be able to detect the fluctuations which occur, and thus to form a judgment as to whether the operation is being carried out satisfactorily. Cases in point are the temperatures of the furnaces used in the manufacture of producer gas, the hot blast used in blast furnaces, and the temperature of cold stores. The recorder designed for this purpose by Callendar is illustrated in Fig. 39, and consists, in principle, of an automatic method of balancing the resistance of the pyrometer, the moving piece that completes the balance carrying a pen at its extremity, so as to make a mark on a sheet of graduated paper fastened round a cylinder which revolves by clockwork. The galvanometer, shown in the upper left-hand part of the illustration, is of the moving-coil pattern, and fastened to the suspension of the coil is a boom, which swings with the coil. The final adjustment of the resistance opposed to the pyrometer is made on a stretched wire, with which the upper part of the pen makes contact. The whole arrangement forms a Wheatstone bridge, of which the arms *b* and *d* (Fig. 35) are represented by the two portions of the stretched wire on either side of the pen. If the temperature of the pyrometer rises, thereby increasing its resistance, the galvanometer coil moves, carrying the boom with it, and causing the end of the boom to complete an electric circuit. The completion of this circuit, by an electro-magnetic device, liberates a detent and sets a train of clock-wheels in motion, which causes the pen to move along the wire, tracing a mark on the paper. When at a certain point on the wire, a balance is again obtained, the galvanometer coil will

Callendar's Recorder.

swing back to the central position, thus causing the b
the electric circuit, and thereby stopping the clockwork
temperature causes the galvanometer coil to swing in th
tion, thereby completing a second circuit, and setting
second train of wheels which move the pen in the oppo
If the temperature remain constant, the pen traces a st



FIG. 39.—CALLENDAR'S RECORDER.

the revolving paper, a fluctuating temperature producing
The divisions on the paper are made to represent actual
and if a drum on which it is wound completes a rev
hours, a continuous record of the temperature during
obtained. Such a record is shown in Fig. 40, which sho
tions of temperature in an annealing furnace during a p

hours, stoked for one half of the time by a workman A, and the remainder by another workman B. The superiority of the stoking of A is made manifest by the record.

The range of temperature covered by the recorder may be arranged by the insertion of suitable resistances, which form part of the instrument. If, for example, the length of the paper represents 100°C. , it is possible, by inserting the correct resistance, to take records varying

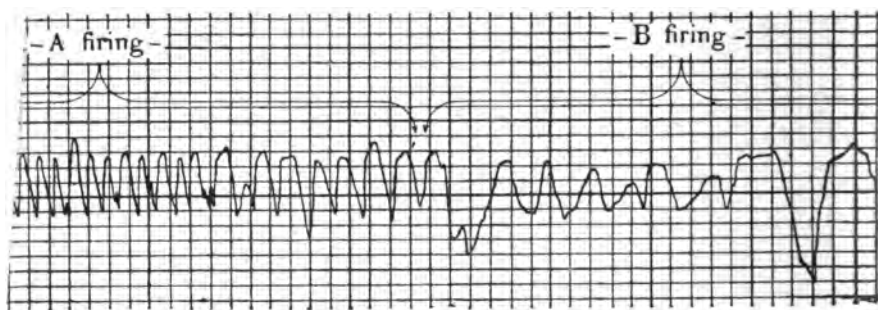


FIG. 40.—RECORD OBTAINED WITH CALLENDAR'S RECORDER.

by 100° at any range up to 1200°C. , such as -50° to $+50^{\circ}$; 800° to 900° , etc. Hence the recorder may be applied to cold stores, ordinary or moderate temperatures, and to furnaces. The arrangement is satisfactory, but costly, which prevents it being more widely adopted. Several other forms of recorder for platinum resistance pyrometers are made similar in principle to that described.

Advantages and Drawbacks of Platinum Resistance Pyrometers.—

The chief advantage of the platinum resistance instrument is its extreme accuracy over a wide range of temperature, if used in conjunction with a reliable indicator or recorder. Very small changes of temperature may be detected, and even when encased in porcelain the pyrometer is fairly responsive to sudden fluctuations of temperature. It has been widely adopted, especially for low temperature work, such as in the operations of brewing, jam boiling, cold storage, etc. It is also good for moderate temperatures, such as those of flue gases and hot blast. A further advantage is that the indicator may be kept in an office at any distance from the pyrometer, provided the leads are the same throughout, as they nullify each other in the measurement. There are many drawbacks, however, attendant on its continued use at very high temperatures. The porcelain cover is very fragile, and costly to replace; if further protected by a steel tube the

instrument is less responsive to sudden changes of temperature. Repeated heating at 1000° C. and over causes a permanent elongation in the wire, altering its resistance in consequence, and causing the indicator readings to be erroneous. The mica supports also deteriorate, and if by any chance metallic vapours enter the pyrometer the platinum is attacked, and the instrument rendered useless. In case of repairs, great skill is required, it being generally necessary to send the apparatus back to the makers, which occasions inconvenience and delay. On the whole, for very high temperature work, the platinum resistance pyrometer must be regarded as of less practical convenience and utility than the thermo-electric instrument, although for lower temperatures it is unsurpassed.

5. *Thermo-electric or Thermal Couple Pyrometers.*—In 1822, Seebeck discovered that the heating of a junction of two different metals forming part of a closed circuit, causes a current of electricity to flow round the circuit. In 1830, Becquerel, using platinum and palladium as the metals, attempted to apply the Seebeck effect to the measurement of temperatures, but with indifferent success. Afterwards Pouillet and others attempted to measure temperatures by the thermo-electric method, but no accuracy or uniformity in results was obtained until 1886, when Le Chatelier showed that if the right metals were employed, the method was capable of giving excellent results. At the present time the thermo-electric pyrometer is probably more used than any other variety.

The two chief laws of thermo-electricity may be stated as follows:—

1. The electromotive force developed by a heated junction depends on the metals used and is independent of the size.

2. If a complete circuit be made of two metals, joined at the extremities, and one junction be heated whilst the other is kept cold, the electromotive force generated is proportional to the *difference* between the temperatures of the hot and cold junctions within certain limits.

In attempting to apply these laws to the production of an instrument for measuring high temperatures, the following conditions must be fulfilled:—

(a) The metals must possess high melting-points.

(b) The electromotive force developed should increase in a uniform manner over the range of temperature embraced by the instrument, and should be reasonably large.

(c) There should be no tendency to oxidation on the part of the metals used.

(d) The metals should be capable of being drawn into homo-

geneous wires, in order that a junction made of any portions of two given pieces may develop the same E.M.F. at the same temperature.

If the temperature to be measured does not exceed 1000°C. , the metals copper, gold, nickel, iron, platinum, palladium, rhodium, osmium, and iridium might be used, provided a junction of the pair selected fulfilled the other conditions. Readings up to 1500°C. would lead to the elimination of all save platinum and the rare metals which have melting-points well above 1500° . At temperatures less than 1000°C. , however, iron undergoes certain molecular changes which lead to the production of minor or parasite currents in the circuit, which are of sufficient magnitude to alter the uniformity in the rise of E.M.F. seriously. This was not known to the early experimenters, some of whom used thermal couples of platinum and iron, and consequently obtained discrepant results. A couple made of iron and copper gives curious results. Up to 280° the E.M.F. shows a fairly steady rise, but with a further increase in temperature it diminishes, and becomes zero; finally an E.M.F. in the opposite direction is set up. Such a couple would therefore be useless for temperature measurement. An objection to palladium is its tendency to absorb hydrogen in large quantities, which alters its thermo-electric properties. Again, iron and copper oxidise readily at temperatures below 1000° , and above this temperature nickel also oxidises, and undergoes molecular changes. It will thus be seen that it is a matter of great difficulty to find a pair of metals which fulfil all the necessary conditions.

The first successful thermo-electric pyrometer was made by Le Chatelier, who found that uniform and accurate connections between E.M.F. and temperature could be obtained by using a couple consisting of platinum, and an alloy of platinum and rhodium. An alloy containing 10 per cent. of rhodium and 90 per cent. of platinum may be made of uniform composition, and is capable of being drawn into fine wire. Coupled with pure platinum, the heated junction furnishes a steadily increasing E.M.F. as the temperature rises. No changes in physical structure or thermo-electric properties occur as a result of the heating, and consequently a second set of observations at given temperatures will give the same results as the first. Moreover, the E.M.F. increases with the temperature to such an extent that a very small rise of temperature may be detected. Neither the platinum nor the rhodium alloy tend to oxidise on heating; both have extremely high melting-points; and, if carefully annealed, wires made from both are quite homogeneous, and any portions of a given pair of wires will give an identical E.M.F. when joined and

heated. Barus and Roberts-Austen afterwards found that equally good results could be obtained with a couple consisting of platinum as one metal, and an alloy of 10 per cent. iridium and 90 per cent. platinum as the other. Pyrometers based on the thermo-electric principle are now made with either of the couples named, and are equally satisfactory.

The couple introduced by Le Chatelier (Pt — Pt + 10 per cent. Rh) furnishes an electromotive force of about 500 micro-volts at 100° C., when the cold junction is kept at 0° C. The same figure is obtained when iridium is substituted for rhodium. At higher temperatures, however, the E.M.F. is not a simple multiple of that observed at 100°; thus at 500° the E.M.F. would not be five times that obtained with the junction at 100°. The two quantities, however, have been found experimentally to be connected by the law

$$\log E = A \log t + B,$$

where E = electromotive force in micro-volts
 t = temperature in degrees Centigrade
 A and B = constants depending on the materials used.

Results calculated from this formula do not differ by more than two or three degrees at any part of the scale from actually observed temperatures. It is therefore possible, by measuring the E.M.F. at two fixed points, to calculate the temperature corresponding to any given E.M.F. by applying the formula, and the results may be checked, if desired, by an experimental determination at another fixed point. This would involve the use of an accurate method for measuring small electromotive forces, and is not necessary in workshop practice, for the purposes of which a good form of galvanometer may be made to indicate the temperature of the junction with great accuracy.

Galvanometers for Use with Thermo-electric Pyrometers.—The best type of galvanometer to employ with a thermo-electric pyrometer is that of d'Arsonval, suitably constructed to give quantitative readings. In these galvanometers the current passes through a coil of wire suspended between the poles of a fixed magnet. The suspension is formed by a strand of metal wire to which the coil is connected, and carries a mirror from which a spot of light may be reflected on to a scale. The axial movement of the coil, caused by the passing of a current, is thus magnified; and the position of the spot of light on the scale, as indicated by the divisions, should be proportional to the strength of the current passing through the coil. Such a galvanometer, when joined to a thermal couple, will give

indications proportional to the E.M.F. existing at the hot junction, and therefore to the temperature ; for, by Ohm's law,

$$E = C R,$$

and consequently if R , the resistance, be constant, the current C will vary directly as E , the electromotive force.

In order to ensure accuracy in this respect, the coil of the galvanometer should be made of wire which shows little variation in resistance when the temperature alters ; suitable materials being manganin, German silver, or platinoid. The coil should have sufficient free space in which to move between the poles of the magnet, and the suspending wire should be strong and yet thin, so as to twist readily. A thin, flattened German silver wire makes a good suspension, or phosphor-bronze may be used. Care must be taken that the suspending wire possess no initial torsion. The type of galvanometer described is shown in use in Fig. 44 (p. 162), in conjunction with a recorder. It may be added that the coil of the galvanometer should have a resistance exceeding 400 ohms, so that the increased resistance of the wires forming the junction, when inserted at different depths in the furnace, does not appreciably alter the strength of the current in the circuit. A series resistance may be added, if required, to ensure this result.

Example.—If the coil of the galvanometer has a resistance of only 50 ohms, and the variation of the resistance of the junction wires is 2 ohms, the latter factor will notably affect the current, as it is equal to $\frac{2}{52}$ of the total resistance. If, however, the coil has a resistance of 800 ohms, the variation due to the junction wires only causes an alteration of $\frac{2}{802}$ th part of the total resistance, and consequently the effect on the current is very small.

In cases where very exact readings are not required, needle galvanometers may be used. Siemens-Halske, Paul, Pitkin, and others have constructed indicators for thermal-couple pyrometers in which the movements of the galvanometer needle over a prepared scale give temperature readings directly, to within 5 or 10 degrees C. Such instruments are correct, within this limit, for the particular pyrometer with which the graduation has been made, but the scale would not be correct for another pyrometer obtained elsewhere. When the scale may be relied on, such indicators possess the advantages of portability and simplicity in use, and consequently have been largely adopted. Crompton's indicator is furnished with several scales, each corresponding to a given temperature of the cold junc-

tion, and obviates the necessity for correcting for variations in this temperature.

Practical forms of Thermo-electric Pyrometers.—A convenient form of pyrometer is illustrated in Fig. 41. The wires from the hot junction J, pass through small fire-clay cylinders, which serve to insulate them, into the wooden handle H, which is made so as to open. The wires are connected to the brass strips S, which pass out

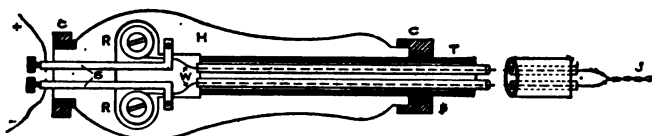


FIG. 41.—THERMO-ELECTRIC PYROMETER.

at the end of the handle and are connected to the galvanometer. A quantity of spare wire is contained on the reels R, R, from which it may be unwound by loosening the strips S. A new junction of the same wires may thus be readily made in the event of damage or corrosion. The distance between the hot junction and the handle is determined by the depth to which the pyrometer is inserted in the furnace, and varies from 5 feet downwards. The wires are contained in a closed steel or porcelain tube T, which serves as a protection from the furnace gases. For temperatures which would cause steel to melt, fireclay or silica tubes may be used. If necessary, the hot junction J may be further protected by a fireclay cap.

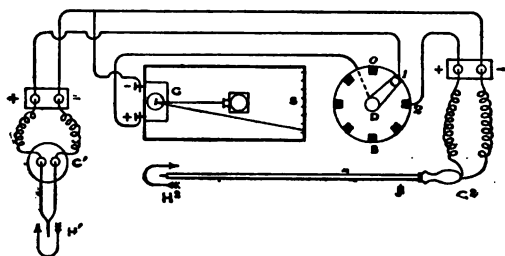


FIG. 42.—METHOD OF USING ONE INDICATOR FOR SEVERAL PYROMETERS.

Fig. 42 shows how the temperatures of a number of furnaces may be read by the use of pyrometers in which identical wires are used, each of which may be connected by a switch to the same galvanometer. H_1 and H are hot junctions, and C_1 and C_2 cold junctions.

Corresponding terminals of each couple are connected to one of the galvanometer terminals, and the other wire of each couple to the positions 1, 2, etc. on the switch B. The movable arm D is connected to the other galvanometer terminal, and serves to connect each pyrometer in turn with the galvanometer. The temperature of any furnace may be thus correctly read, provided the junctions are in all respects identical.

The wires at the hot junction should be fused together, as, if merely twisted, they tend to become loose on heating. This may be done by means of the oxy-hydrogen flame. If the temperature is never to exceed 1000°C. , the couple may be soldered together in a Bunsen burner by means of a small quantity of gold, which will not alter its thermo-electric properties.

Standardising a Thermo-electric Pyrometer.—The preparation of the scale of temperatures in connection with the pyrometer demands considerable care, especially when the scale is to be used as a standard for the comparison of other pyrometers. The wires forming the junction should first of all be annealed by passing a current of electricity through them so as to heat them to whiteness. The temperature of the cold end of the pyrometer should be the same as that which will obtain when in actual use, and the total resistance of the circuit must also be identical with that possessed when in use. The latter point is of great importance when long leads are used to connect the pyrometer to the galvanometer or indicator. When these precautions have been taken, the pyrometer is placed successively in the following, and allowed to remain for a sufficient length of time to enable the spot of light to become stationary; the position on the scale then corresponds to the known temperature of the surroundings of the pyrometer :—

				$^{\circ}\text{C.}$	$^{\circ}\text{F.}$
Steam from boiling water	.	.	.	Temp. = 100	212
Tin at the setting-point	.	.	.	" = 232	449.
Lead ,, ,,	.	.	.	" = 327	620
Zinc ,, ,,	.	.	.	" = 419	786
Antimony ,,	.	.	.	" = 632	1169
Common salt ,,	.	.	.	" = 800	1472
Copper (uncovered) ,,	.	.	.	" = 1062	1943

The above form a set of cheap standards, suitable for a workshop calibration. Any of the fixed points given on page 138 may be chosen, however, if desired. The steam point may be determined by boiling water in a flask, and inserting the pyrometer in the neck, into which it must fit loosely, so as to allow a free escape for the steam. To determine the setting points of the various substances,

a quantity is melted in a graphite or "salamander" crucible in a gas furnace, and the pyrometer inserted in the centre of the molten mass, which is then allowed to cool. As the temperature falls, the spot of light on the scale moves nearer its zero, but at the setting point remains stationary for some time. This is owing to the fact that in the act of solidification latent heat is disengaged, sufficient to maintain a stationary temperature for an appreciable time. Hence the position at which the spot of light remains at rest represents the

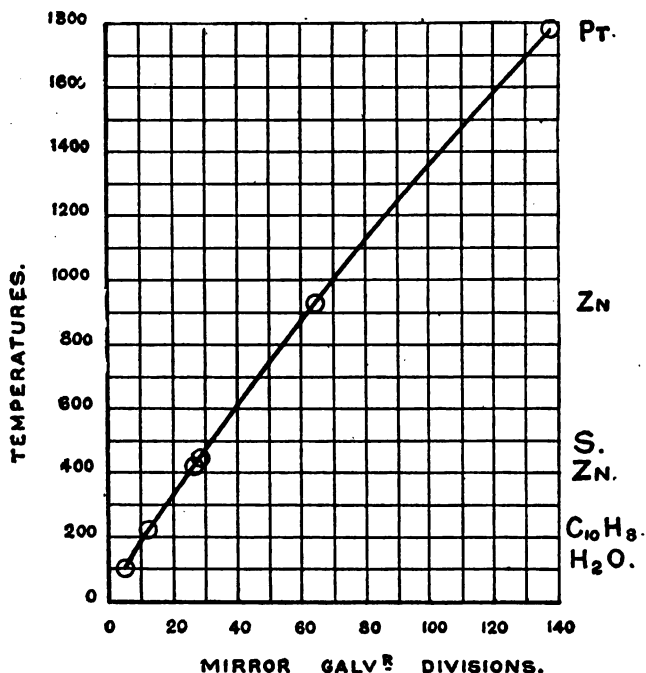


FIG. 43.—CALIBRATION CURVE FOR THERMO-ELECTRIC PYROMETER.

freezing point of the substance. A quantity of pure materials should be kept for the purpose of standardisation, as even small amounts of impurities notably alter the freezing points.

A curve may now be drawn connecting temperatures with deflections on the galvanometer scale, from which intermediate readings may be obtained. The zero of deflection will correspond to the temperature of the cold junction. Fig. 43, which represents a calibration curve for a platinum-rhodium alloy couple, is an ex-

M

ample of this method of graduation, the curve passing smoothly between the points. The platinum point may be obtained by heating until the couple melts and breaks, the maximum position of the spot of light being noted. The curve is produced regularly until it cuts the ordinate corresponding to the maximum deflection, and the temperature thus obtained by extrapolation. The determination of the platinum point, however, is not necessary in practice, and would, of course, destroy the junction. From the curve it will be seen that 80 scale divisions were equal to 1130°C. ; 40 divisions to 610°C. ; and so on. The cold junction in this case was kept at 0°C.

From the standard scale so obtained, others may be graduated by comparison. Any number of pyrometers, if made of the same wire as the standard, may be tested by switching on to the standard instrument, when the temperature shown by each on its own indicator should be made the same as that registered by the standard scale. A whole installation of pyrometers may thus be kept in complete unison, provided the cold-junction temperatures are constant.

Recording Thermo-electric Pyrometers.—For the purposes of the Alloys Research Committee, Roberts-Austen devised the recording arrangement shown in Fig. 44. The galvanometer G is enclosed

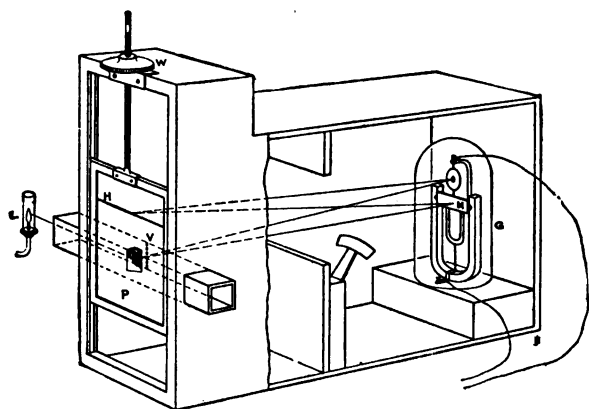


FIG. 44.—ROBERTS-AUSTEN RECORDER.

in a box, and a spot of light is thrown from the lamp L (a Welsbach burner is preferable) on to the suspended mirror by means of a reflecting prism. The spot of light is reflected on to a sensitised plate or paper P, which may be moved up or down at any desired

rate by means of clockwork geared to the wheel W. If the temperature of the thermal junction remain steady, the spot of light reflected from the galvanometer mirror would also be steady, and the discoloration of the paper would take the form of a straight line. Continuous fluctuations of temperature would produce a zig-zag line, and by heating the junction to known temperatures the number of degrees corresponding to a given deviation of the spot of light may be determined, and the paper divided accordingly. A complete record over a given period is thus obtained. To test the accuracy with which the plate moved, Roberts-Austen placed a fixed mirror, M, across the galvanometer magnet, so that the reflected ray from it fell on the sensitised plate. A T-shaped interrupter was placed in the centre of the box, actuated by accurate clockwork, which caused it to rise periodically and shut off the reflected ray from the mirror M. The line traced on the plate was then beaded, and as the interruptions took place at regular intervals, the beading was spaced out regularly when the motion of the plate was uniform, and served as a test of the mechanism actuating the plate. In the modern commercial instrument the plate is replaced by a drum, revolving by means of clockwork, a strip of sensitised paper being fastened on the drum to receive the impression of the spot of light.

A great drawback to the use of this recorder is the necessity of a dark room in which to develop and fix the photographic record, and the labour entailed in this process. Accordingly, many attempts have been made to obtain records in ink, but the great difficulty to be overcome is that the needle or any moving part of the galvanometer cannot be kept continuously in contact with a paper, owing to the friction introduced opposing the movement. Various arrangements for periodical contact of a pen attached to the moving part have been devised, the pen making a dot on the paper, and then being set free to enable the moving parts to attain the correct position before making another contact. A beaded line is thus obtained, which indicates the position of the needle or moving coil at any time, and which therefore constitutes a continuous record of the temperature. The latest and simplest of intermittent contact recorders is the "Thread recorder," made by the Cambridge Scientific Instrument Company. The action of this instrument is illustrated in Fig. 45, where B is the galvanometer suspension, to which a boom A is attached. By means of a cam E, rotated by clockwork, a chopper-bar D is periodically pressed on to the boom A, causing the boom to descend and depress an inked thread G, on to the paper wound round the cylinder C. Where the thread

touches the paper a dot is made, and the contact may be repeated every half-minute, producing a nearly continuous line on the paper. The cylinder C makes one revolution in 25 hours, and the temperature during that period is thus accurately recorded. A scale of temperatures may conveniently be fastened to the front of D for direct reading at any moment. The depression and liberation of the boom are so gently performed by this mechanism that the galvanometer coil, when freed, comes to its proper position in a few seconds. The thread is kept moist by the use of a winding

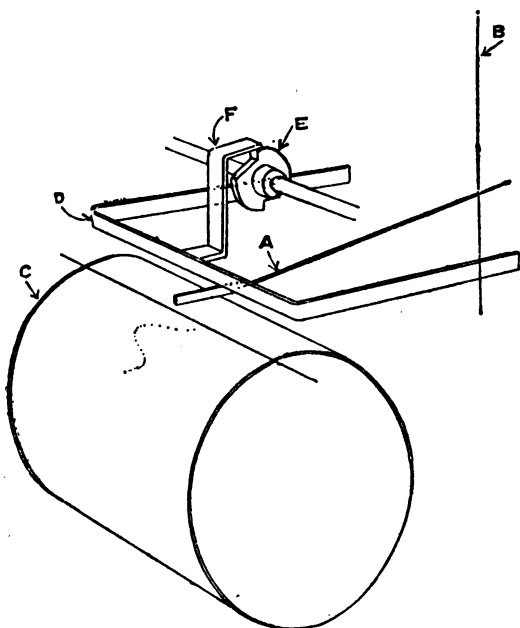


FIG. 45.—PRINCIPLE OF THREAD RECORDER.

mechanism, which passes it through an ink-well. The thread recorder solves the problem of a suitable ink recorder for a thermo-electric pyrometer, and is equally useful in connection with a radiation pyrometer. The actual instrument is shown in Fig. 46.

Advantages and Drawbacks of Thermo-electric Pyrometers.—One of the chief advantages of thermo-electric pyrometers is that a reading may be taken on a scale or indicator at any moment, without the necessity of any adjustment. They may also be used for higher temperatures than is permissible with a platinum-resistance pyrometer,

it being possible to measure temperatures of 1500°C. (2732°F.) and upwards by their use, the upper limit being that at which the insulation of the wires fuses or attacks the metals. By passing the wires through small silica tubes, and surrounding the whole with a larger silica tube, temperatures approaching the melting point of platinum may be read. In the event of a junction being damaged, a new one may be rapidly made, no great skill being requisite. The thermoelectric pyrometer is therefore to be preferred in cases where a certain amount of rough usage is unavoidable.

The chief drawback is the alteration in E.M.F. given by the couple on prolonged heating above 1000°C. ; ten hours at 1100°C. producing an increase of 0.5 per cent. in a Pt-Rh couple. The original

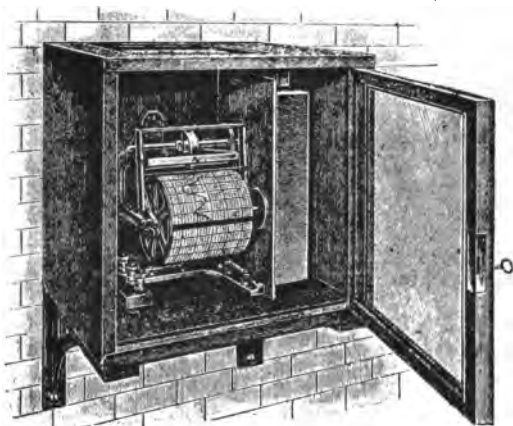


FIG. 46.—THE THREAD RECORDER.

value may be restored by annealing at a full white heat, and, in general, the alteration in E.M.F. is small in a well-annealed couple. The metals are liable to be corroded under certain conditions, as described in connection with the platinum resistance pyrometer. The Pt-Ir couple is liable to injury in either a reducing or oxidising atmosphere on prolonged heating at 1100°C. and over, the E.M.F. falling off in some cases by 12 per cent. At lower temperatures, if well annealed, the Pt-Ir couple gives good results. Above 1100°C. , therefore, the Pt-Rh couple should be used. Finally, the accuracy of the readings is less than that obtained with the resistance pyrometer, although the approximation to the correct temperature yielded by the thermoelectric method is sufficient for all practical purposes.

Thermal Couples for Extremely High Temperatures.—Since the commercial introduction of the electric furnace, a means of measuring temperatures beyond the melting-point of platinum has become desirable. A couple consisting of the metals iridium and ruthenium has been used by Heræus for readings up to 2100°C. , but the graduation, which must be made by extrapolation, is of doubtful accuracy. The couple, moreover, is extremely brittle, and therefore liable to injury, and cannot be said at present to be of any great use commercially. It is possible that metals of still higher melting points, such as tantalum and tungsten, may be utilised in this connection in the future. Probably more is to be hoped for in the couples made of Nernst filament materials, of different composition, as suggested by Harker. These consist of silicates of the rare earths, and are pyro-conductors, that is, conduct electricity only when heated, and two filaments when joined and heated give rise to an E.M.F. when of different composition. As the melting-point of a Nernst filament is much above that of platinum, it may be possible by this means to read temperatures as high as 2000°C. For higher temperatures still, recourse must be had to optical or radiation methods.

Thermal Couples for Low Temperatures.—The drawbacks attendant on the use of most metals for thermo-electric couples at high temperatures, such as melting, oxidation, molecular changes, etc., do not apply at low temperatures. Consequently it is found possible to measure low temperatures by the aid of suitable couples such as copper-constantan, iron-constantan, copper-German silver, etc., the couples giving a high E.M.F. being chosen. When the junction is colder than the rest of the circuit, a reverse E.M.F. is set up, proportional to the difference of temperatures as in the converse case. Professor Dewar has employed a copper-German silver couple to measure extremely low temperatures, the galvanometer being standardised by comparison with a gas thermometer, and a convenient means of determining very low temperatures thus obtained. For obtaining temperatures in places where thermometers would be unsuitable, such as in the cylinders of engines when working, copper-constantan thermal junctions are largely used, and prove highly satisfactory.

Practical Management of a Pyrometer Installation.—A brief description of the methods adopted in the Royal Gun Factory, Woolwich Arsenal, will serve to indicate the uses and practical control of a commercial pyrometric installation. The operations include the tempering of gun-tubes, lead baths for the treatment of specimens used for testing, gas producer furnaces, equipment for determining the critical points of steel, and other processes. Thermo-electric

pyrometers are used, in conjunction with Holden-d'Arsonval galvanometers of about 800 ohms resistance, the metals of the couple being platinum and iridium alloy. A large quantity of each wire is obtained of uniform composition, so that every junction may give the same E.M.F., and may be replaced, when necessary, by an exactly similar junction. A standard instrument, carefully calibrated, is kept in the metallurgist's office, and each pyrometer may be connected to it. The standardising of the pyrometer scales is carried out *in situ* by noting the scale reading at different temperatures, and obtaining the degrees corresponding to each by switching on to the standard, due allowance being made for the cold-junction temperature known to exist when in use. Each set of furnaces is in telephonic communication with the office, and when an operation is ready to carry out, as indicated by the furnaceman's own scale, the office is rung up and the pyrometer switched on to the standard, as a check. If both readings agree, word is given to proceed.

The galvanometer mounting shown in Fig. 47 is used to prevent vibration and consequent difficulty in reading. It consists of a strong brass tripod, from the rim of which the galvanometer is suspended on three spiral springs, which the weight of the galvanometer keeps $\frac{1}{2}$ in compression. That is, if the galvanometer weighs 6 lb., each spring would require 6 lb. to compress it so that the coils touch. The adjustment of the spot of light is obtained by means of the screws at the top of the suspending rods. A galvanometer so suspended is singularly unaffected by external vibrations, and will give steady indications in the vicinity of steam-hammers, or railway lines over which loaded wagons are running.

Each pyrometer and scale is checked every morning by placing the pyrometer in a bucket of boiling water, and taking the reading. Any serious defect is at once detected, and an assistant sent to execute the necessary repairs. As a check on the standard scale, which might accidentally be displaced, a pyrometer is kept in steam in the office, which may be switched on to the standard galvanometer,



FIG. 47.—HOLDEN AND LAMBERT'S
ANTI-VIBRATION MOUNTING
FOR GALVANOMETERS.

and thus serves to detect any displacement which may have occurred by the erroneous reading the scale would then show. The hole in the furnace through which each pyrometer passes is luted with clay, as otherwise the junctions at the head would be unduly heated.

Records are taken in special cases only, the Roberts-Austen recorder being used, suspended in the same manner as the galvanometers to obviate vibrations, which would be specially objectionable in this case. The records are taken on sensitised paper.

The excellent results obtained by the use of this equipment are a testimony to its value. What formerly was a matter of doubtful judgment by a workman's eye is now replaced by a method of precision, and a variety of operations are now carried out not only with certainty of success, but with greater economy, owing to the complete control exercised by the metallurgist over all the work conducted in the numerous furnaces.

(6) *Heat-Radiation Pyrometers.*—The great advantage of a pyrometer which would indicate the temperature of a furnace from a distance has long been recognised. Any form of pyrometer continuously subjected to the heat and corrosive action of the gases in a furnace is bound to deteriorate, and so necessitate repairs or replacement. Further, the range of a pyrometer, when placed in a furnace, is limited by the melting point of its materials, whereas an instrument used at a distance would not be subject to this disadvantage. Work in this direction was attempted by Pouillet, Violle, and others, but the results were so discordant that the method was regarded as absolutely unreliable. Thus Pouillet found for the temperature of the sun a value of 1300°C. ; Violle's results indicated 1500°C. to 2500°C. , whilst Secchi actually obtained a figure running into millions. All these discrepancies, however, were due to imperfect knowledge of the laws of heat-radiation, which are now better understood, with the result that reliable temperature indications may be obtained from observations of radiant heat.

A full discussion of the principles governing the radiation of heat will be found in Chapter XIX., and it is only proposed at the present juncture to indicate the basis upon which a satisfactory heat-radiation pyrometer may be constructed. The amount of energy radiated by a "black body," according to the Stefan-Boltzmann law, is proportional to the fourth power of the absolute temperature. Expressed as a formula this law takes the form

$$E = K (T^4 - T_1^4)$$

where E = the total energy radiated by the body at absolute tem-

perature T to surroundings at an absolute temperature T_1 , and K is a constant which depends upon the units employed.

The correctness of this formula has been amply verified by experiment. Thus in a series of observations by Waidner and Burgess at temperatures ranging from 850°C. to 1450°C. , the values calculated from the formula differed by less than 1 per cent. from the actual readings of a thermal-couple pyrometer. It should be borne in mind, however, that the formula is only strictly correct for "black-body" radiations. An "absolute black-body" is one which absorbs all the radiations which fall upon it, and neither reflects nor transmits any, and is nearly realised in practice by coal, carbon, and heated metals which become coated with black oxides, such as copper and iron. If, therefore, any practical means can be found of measuring the proportionate amounts of energy radiated by such heated surfaces at different temperatures, it is possible to calculate the temperature itself from the Stefan-Boltzmann law. The method, however, need not be restricted to black surfaces, for, as Kirchhoff showed, the interior of an enclosure kept at a constant temperature gives true black-body radiations. If, for example, a metal box be surrounded by steam, and a hole be made in the side, radiations passing from the interior through the hole will be black-body radiations in terms of the definition. If we consider a portion of the wall opposite the hole, the energy radiated from this spot must be equal to that which it absorbs from its surroundings, or its temperature would alter. But equality of temperature in an enclosure involves equality in the amounts of energy radiated and absorbed by each portion, therefore the spot absorbs all the energy it receives, and, irrespective of the nature of its surface, behaves as an absolute black body. Hence the radiations received from the interior of a furnace, at constant temperature throughout, may be regarded as black-body radiations, and the temperature deduced by applying the fourth-power law.

If the energy radiated by a surface which is not a black body be measured, and the temperature calculated on the assumption that the Stefan-Boltzmann law also applies in this case, a result lower than the truth will be obtained, owing to the inferior radiating power of the surface. At an actual temperature of 1500°C. , for example, a platinum surface would only give a calculated temperature of 1320°C. But as the radiating power of the platinum surface is constant under given conditions, it follows that whenever the temperature, as deduced from the radiation law, is 1320°C. , its true temperature will be 1500°C. The thermal condition of platinum is therefore defined

with the same certainty as if a true reading were taken by another method. Whilst this holds true in general for surfaces not altered by heat, bodies which oxidise possess a varying radiating power, if not enclosed. Thus if a block of steel be heated, and removed from the furnace, the temperature indicated by the radiations from its surface depend upon the thickness of the film of oxide which forms over it. This film of oxide cools rapidly, and the indication obtained affords no clue to the temperature of the mass. The only safe procedure is to measure the radiations received when the steel is under black-body conditions; that is, when inside the furnace. Many failures have resulted owing to the assumption that the apparent temperature—wrongly called “black-body temperature”—bears in all cases a constant relation to the true reading. This is only true for unaltering surfaces, such as platinum.

Féry's Heat-Radiation Pyrometers.—Two forms of heat-radiation pyrometer, each devised by M. Féry, represent the practical realisation of the application of the fourth-power law to temperature measurement. In the first form a copper-constantan thermal couple, soldered to a copper disc, is placed in the focus of the object-glass of a telescope, which thus behaves like a burning-lens. Between the object-lens and thermal couple a diaphragm is fixed, which ensures that the cone of rays falling on the couple is not changed in size by focusing the instrument. The image of the heated body is sharply focused on the thermal couple, which is connected through the tube of the telescope to a Meylan-d'Arsonval galvanometer. The temperature attained by the thermal couple, and consequently the deflections of the galvanometer, depend upon the amount of radiant heat passing into the telescope; and this, in turn, depends upon the absolute temperature of the hot substance. If the graduations of the galvanometer scale are of equal value, and the temperature T , corresponding to a given reading R , be known, the value to be attached to any other reading R_1 , may be found from the relation

$$\frac{R_1}{R} = \left(\frac{T_1}{T}\right)^4,$$

or

$$T_1 = T \sqrt[4]{\frac{R_1}{R}}.$$

Hence a temperature scale may be readily constructed from one exact observation at a known temperature as a starting-point. The drawback to the use of this pyrometer is that a quantity of the radiant

heat is absorbed by the glass objective, the amount absorbed varying with the temperature. If the objective be made of fluor-spar instead of glass, this difficulty is overcome for temperatures above 900°C ., as beyond this limit the ratio of absorbed and transmitted radiant energy is constant in the case of fluor-spar. Hence the arrangement is restricted to temperatures above 900°C .; and as fluor-spar crystals large enough to make lenses are difficult to procure, it is necessary to use a glass objective, and to standardise the pyrometer by comparison with a special instrument which possesses a fluor-spar object-lens. The range 700°C . to 900°C . embraces the temperatures at which many important processes are conducted, and consequently the first form of Féry's heat-radiation pyrometer was not widely adopted.

In the later form of instrument, the difficulty caused by the absorption due to the glass is entirely overcome by the use of a concave mirror which brings the rays to a focus on the copper-constantan couple. Figs. 48 and 49 show the construction of the pyrometer as

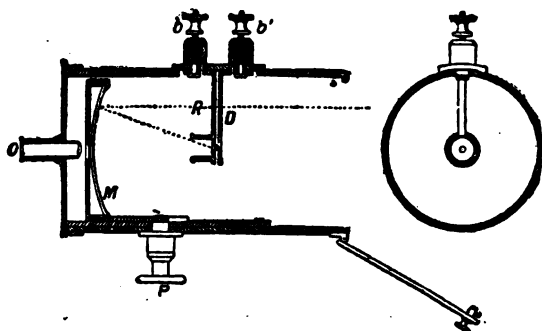


FIG. 48.—FÉRY'S RADIATION PYROMETER, SECTION.

now made for commercial use. In Fig. 48, M is the concave mirror which may be moved backwards and forwards by a rack-and-pinion movement controlled by the milled-head P. In early forms this mirror was made with a silvered surface, which tarnished in use, and deteriorated in reflecting power; but by gilding this trouble was overcome. The thermal couple is connected to two fixed brass strips, R and D, each of which is connected to one of the terminals b , b_1 on the exterior of the instrument, these terminals being insulated from one another. The thermal junction is placed at the focus of the eye-piece, O, and appears as a circular black disc when viewed through the small hole in the centre of the mirror. The image of the source of heat must be brought into the focal plane of the eye-piece O, so as

to overlap the thermal junction, and this may be accomplished by moving the mirror M backwards or forwards, according to the distance of the pyrometer from the furnace. To secure exact focusing, the image of the hot body formed by the concave mirror is reflected to the eye-piece by the aid of two small plane mirrors placed near the couple, each of which reflects one half of the image; and it is so arranged that when the focus is correct, the separate halves of the image are continuous, but are discontinuous when the focus is not correct. The rise in temperature of the couple produces an E.M.F. which is registered by a Meylan-d'Arsonval galvanometer, and temperatures are deduced from the fourth power law, as previously described.

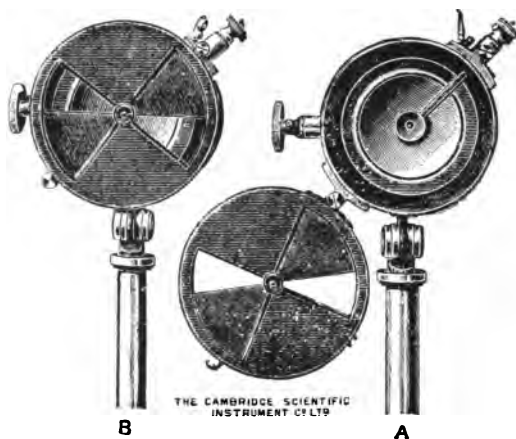


FIG. 49.—FÉRY'S RADIATION PYROMETER, END VIEW, SHOWING REDUCING DIAPHRAGM.

The galvanometer is furnished with two scales, over which the pointer moves, one of which is for use with the full aperture, and registers from 600°C. to 1300°C. , whilst the second scale is used in connection with the diaphragm shown in Fig. 49, which, when swung over the end of the tube cuts off a definite fraction of the total radiation, and enables temperatures to be read which, with full aperture, would send the needle off the scale. The higher scale reads from 1000°C. to 2000°C. The range of temperature recorded might also be increased by shunting the galvanometer and maintaining a full aperture, provided the temperature of the junction (which, with the present arrangement, never exceeds 110°C.) is not unduly raised.

The distance of the pyrometer from the hot body is immaterial so

long as the image completely overlaps the thermal junction. The limiting distance, for a given pyrometer, may be calculated from the well-known optical principle—

$$\frac{\text{size of image}}{\text{size of object}} = \frac{\text{distance of image from mirror}}{\text{distance of object from mirror}}$$

Example.—If the diameter of the thermal-couple disc be $\frac{1}{8}$ inch, the diameter of the object viewed 12 inches, and the distance of the mirror from the thermal-couple 3 inches when the object is correctly focused, the limiting distance will be reached when the size of the image is equal to that of the thermal-couple, that is, has a diameter of $\frac{1}{8}$ inch. Inserting values in the above ratio,

$$\frac{\frac{1}{8}}{12} = \frac{3}{x}$$

from which $x = 432$ inches or 36 feet.

The maximum distance from the source of heat is given with each instrument, and is usually 1 yard for every inch of diameter of the heated aperture viewed. On approaching the source of heat, the amount of radiation received by the mirror will be greater in the inverse proportion of the square of the distances. Thus at 6 feet distance the radiations will be four times as great as those received at a distance of 12 feet. But at the nearer distance a larger image is formed, which greatly overlaps the junction, so that at a distance of 6 feet the proportion of the radiations which impinge on the junction are only $\frac{1}{4}$ of the proportion which obtains at a distance of 12 feet. Hence, within the limit given, the actual amount of radiations striking the couple is constant at all distances, and the same temperature is recorded.

In using the heat-radiation pyrometer it must always be borne in mind that the scale is graduated with respect to black-body radiations. Correct readings will be obtained if the instrument be sighted on the object whilst in the furnace, or by inserting a fireclay tube, closed at one end, in the furnace, and sighting the closed end. In either case black-body conditions are realised. On the other hand, the indications obtained from the surface of molten metal in a ladle are below the truth; and if fumes arise, as in the case of alloys containing zinc or lead, the radiations are seriously interfered with, and the reading is far too low. Smoke in a furnace similarly retards the radiations, and consequently care must be exercised that no solid particles intervene between the hot body and the pyrometer.

Records of temperature may be obtained with this pyrometer when used in conjunction with a "Thread" or other intermittent recorder, or with a Roberts-Austen photographic recorder, the procedure being identical with that adopted in connection with thermo-electric pyrometers.

Advantages and Drawbacks of Heat-Radiation Pyrometers.—The lens form of heat radiation pyrometer is little used, owing to its lower limit (900°C.) seriously restricting its commercial utility. The mirror form, which is capable of reading from 600°C. —or lower if necessary—to an indefinitely high temperature, has become a formidable rival to other forms of pyrometer. The deterioration which must inevitably take place in any instrument when constantly heated in a furnace is entirely avoided, as no part of the instrument attains a higher temperature than 110°C. The unlimited range qualifies this pyrometer for use in connection with electric furnaces, and other high temperature operations which are beyond the compass of instruments which must be placed in the source of heat. It requires no skill in use, and the indications are rapid. It has the further advantage over pyrometers fixed in position that it may be focused on any part of a furnace, or any object in it, and is thus not restricted to recording the temperature at one part only. For recording purposes it may be mounted opposite a tube with a closed end, inserted to any desired depth in the furnace, and focused on the end of the tube.

The chief drawback is that an installation worked from a central standard, cannot be made with these pyrometers, as complete identity—optical and otherwise—is practically impossible to attain. Each pyrometer will only yield true readings on its own specially standardised indicator.

7. *Optical Pyrometers.*—An investigation of the light proceeding from a luminous object may, with proper precautions, furnish a clue to the temperature of the object. An instrument working on this principle would possess the same advantages as a heat-radiation pyrometer in the respect that its indications could be obtained at a distance from the source of heat. Up to the present, however, the various forms of optical pyrometers introduced by different investigators have received little practical application in the workshop, although of service in the laboratory for the determination of the temperature of small luminous sources, such as the filaments of incandescent and Nernst lamps, and the crater of the arc lamp. The drawback to the use of these pyrometers in a workshop is that considerable skill is necessary in obtaining correct readings, and that a delicate adjustment of parts is necessary, rendering the instruments extremely susceptible

to rough usage. Space will only permit of a description of the method adopted in connection with the more important types, and for details the reader is referred to special treatises on the subject.

The colour changes experienced by a substance as its temperature rises are well known, and the temperatures corresponding to different colours were found by Pouillet as follows :—

	°C.		°C.
First visible red . . .	525	Dull orange . . .	1100
Dull red . . .	700	Bright orange . . .	1200
Turning to cherry . . .	800	White . . .	1300
Cherry proper . . .	900	Brilliant white . . .	1400
Bright cherry . . .	1000	Dazzling white . . .	1500

These colours are used to form a judgment in conducting many workshop operations, such as tempering chisels, forging steel, etc., but the temperatures attached to them are uncertain, as no two persons form quite the same judgment of the colour. At a dull red heat the change is most sensitive, a rise of 20° C. being detectable to a trained eye; thus the recalescence of a piece of steel between 700° and 800° C. is readily seen. It is the uncertainty of judging colour changes with even an approximation to accuracy that has led to the necessity for pyrometers.

The photometric measurement of the total luminosity cannot be relied upon to furnish a clue to the temperature, as bodies at the same temperature may possess widely differing luminosities. If it be attempted to obtain the temperature of a hot space by measuring the candle-power of a piece of platinum placed in the space, the changing colours of the platinum render the method unreliable. Definite results can only be obtained by measuring the intensity of a radiation of given wave-length, or by comparing the intensities of radiations of definite wave-lengths. Both these principles are utilised in the construction of optical pyrometers.

Le Chatelier's Optical Pyrometer.—In this instrument the intensity of the red radiations of the hot body or space are compared with those received from a standard source by means of a special kind of photometer. The hot body is viewed through a telescope, at the object end of which is placed a piece of red glass, and also an iris diaphragm which regulates the amount of luminous radiation received by the eyepiece. A branch at right angles to the telescope contains a standard lamp, the light from which, after passing through a piece of red glass, is reflected by a mirror placed at 45° into the eyepiece, so as to appear side by side with the image of the hot body.

By adjusting the diaphragm, and interposing other glasses when necessary, the two images may be made equally luminous. The determination of the temperature from these observations is a complicated matter, involving measurements of the absorption coefficient of the glass, the emissive power of the source of luminosity, and a knowledge of the connection between temperature and the intensity of red radiations. Le Chatelier was enabled, as a result of his investigations, to prepare a table for the pyrometer from which temperatures could be deduced from the number of absorption glasses interposed, and the diameter of the diaphragm when equality of tint is obtained. The figure given by this pyrometer for the temperature of the arc lamp is 4100°C. , or 500° higher than that indicated by the heat-radiation pyrometer. In Féry's modification a fixed diaphragm is placed in the tube of the telescope, so that the angular aperture is fixed, and the result made independent of the distance of the furnace within considerable limits. The iris is replaced by a pair of absorbing glass wedges, which may be pushed over one another and thus caused to interpose any desired thickness of absorbing glass between the object and the telescope lens. The calibration is based on the law that the thickness of wedge interposed varies inversely as the absolute temperature.

The Wanner Pyrometer.—In this instrument a standard source of light is obtained by illuminating a ground-glass surface by means of a small incandescent electric lamp. Light from this surface is passed through a direct vision spectroscope, furnished with a diaphragm which cuts off all but a band in the red portion of the spectrum. By means of a second slit in the end of the instrument, light from the source under observation is similarly treated. The relative intensities are measured by a polarising arrangement, and the temperature, deduced from the angle through which the analyser must be turned to produce equality of tint in the light received from the two slits and a knowledge of the black-body temperature of the standard, is marked on the circumference of a dial which rotates with the analyser. As the incandescent lamp deteriorates with use, it must be compared from time to time with a standard amyl acetate lamp, and the voltage increased to bring its illuminating power to that which it possessed when the instrument was graduated. Owing to the great loss of light caused by the optical arrangements, certainty of measurement cannot be obtained below 900°C. (1650°F.).

Holborn's Optical Pyrometer.—The principle of this instrument is to make a comparison between the luminosity of the filament of a small incandescent electric lamp, connected to a rheostat and milli-

ammeter, and that of the source. To this end the filament of the lamp is placed in the focal plane of a telescope objective, and may be viewed through an eye-piece in which a red glass is placed. If the filament be at a different temperature to the object, it will be seen superposed on the image of the hot source. By varying the rheostat, the luminosity of the filament may be altered until it is no longer visible on the bright background. The current passing through the lamp is then noted, and the temperature obtained from the relation found to exist between the temperature of the lamp filament and the current. This relation takes the form

$$C = a + bt + ct^2,$$

where C = current, t = temperature, and a , b , and c = constants depending on the kind of lamp used. This method has been found to give excellent results up to 1500°C .

Mesuré and Nouel's Pyrometer.—In this apparatus a piece of quartz, cut perpendicularly to the axis, is placed between two Nicol prisms; an arrangement which serves to cut out the central portions of the spectrum. The relative intensities of the red and green portions of the spectrum are then used to indicate the temperature, the green portion becoming relatively brighter as the temperature rises. One of the Nicol prisms, which serves as an analyser, is fastened to a rotating disc, which is graduated. On turning the analyser a red colour is observed in one direction, and a green colour in the other. The intermediate position, where a neutral tint is obtained, alters with the temperature of the luminous source, and is determined by the relative brightness of the red and green portions of the spectrum. The division on the rotating disc which is opposite a fixed mark is noted when the intermediate tint is obtained, and the temperature read from a table provided. This table is prepared by sighting the pyrometer on a surface, the temperature of which is varied, and noted at each reading by means of a thermo-electric pyrometer. The Mesuré and Nouel pyrometer is used in cases where a rapid, approximate result is desired; an error of judgment in deciding the neutral tint might make a difference of 100°C . or more in the reading.

Advantages and Drawbacks of Optical Pyrometers.—The ability to measure a temperature from a distance is a strong point in favour of optical pyrometers, and there need be no upper limit to the temperature measured if the laws of luminous radiations are fully known and used in the graduation of the instrument. As the use of the electric furnace extends, and operations at extremely high tempera-

tures become more common, it is safe to predict that optical pyrometers will be more extensively used than at present. Many important researches have already been carried out by the aid of these instruments, which, until the introduction of the heat-radiation pyrometer, furnished the only means of measuring temperatures beyond the scope of a thermo-electric pyrometer.

The chief drawbacks are the fragile character of the instruments, the delicate adjustments required, and the skill necessary to obtain correct readings; all of which militate against their extended use in the workshop. In many of the forms, moreover, the temperature scales cannot be regarded as certain; and the maintaining of a standard illuminating surface is bound, in ordinary practice, to give rise to trouble. They are not adapted for obtaining continuous temperature records.

8. *Linear Expansion Pyrometers.*—Brogniart and others designed pyrometers based on the expansion of a rod of iron, free to move at one end only. The elongation was multiplied by levers, the terminal lever causing an index-hand to move round a dial. From the known coefficient of the expansion of the iron, or by comparison with a standard, the dial could be marked to represent degrees. Pyrometers based on this principle are still made, largely for use in bakers' ovens. A rod of iron, surrounded by a porcelain or fire-clay tube, touches the end of the latter at one of its extremities, and is free to move at the other and cause an index to move over a dial. The difference between the expansion of the iron rod and the enclosing tube is thus made to indicate the temperature. In another form the index is actuated by a rod of carbon placed in an iron tube. Such pyrometers cannot be regarded as in any sense exact, as the coefficients of expansion of the substances are not uniform at all temperatures, and alter in value on continuous heating. They are not intended for use above 700°C ., but at lower temperatures form a sufficiently exact guide in many operations, and in addition are cheap and require no manipulation. Much greater certainty can be obtained by the use of these instruments than by trusting the eye.

9. *Fusion Method of Obtaining Furnace Temperatures.*—Where intermittent readings of a furnace temperature suffice, and it is not desired to make the necessary outlay for a pyrometer, the fusion method furnishes a cheap and fairly accurate means of obtaining the desired readings. A series of substances differing progressively in melting-point are obtained, and by placing them in the furnace until the temperature existing is attained, some will be found to melt, whilst others remain solid. The furnace temperature may then be obtained

from the known melting-points of the substances, with an accuracy depending upon the interval between the successive fusion temperatures. As an example of the method, the following salts may be chosen :—

<i>Salt.</i>	<i>Melting Point.</i>
1 molecule common salt + 1 mol. potassium chloride	650° C.
common salt	800
anhydrous sodium carbonate	850
anhydrous sodium sulphate	900
sodium plumbate	1000
anhydrous potassium sulphate	1070
anhydrous magnesium sulphate	1150

If, in the furnace, it be found that the first two in the series have completely melted, whilst the sodium carbonate is intact, it is then known that the furnace temperature exceeds 800° C., but is less than 850°. A knowledge of these limits often suffices.

Instead of salts, a prepared series of metals and alloys may be used. It is not necessary to place the whole series in the furnace, but only those which are known by experience to have melting-points near to that of the furnace temperature.

*Sege*r* Pyramids or "Cones."*—The fusion method has been brought to a high degree of accuracy by Sege*r* of Berlin. Small triangular pyramids, 50 millimetres in height, each side of the base measuring 15 millimetres, are made of silicates of varying composition. The pyramids are numbered from "38," which melts at 1890° C., to "022," which melts at 590° C.; a range of 1300° C. being thus comprehended. Altogether 60 different pyramids are used, differing in melting-points by intervals of 20° from 1890° to 950°, and afterwards by intervals of 30°. The shape is well designed for observations of fusion, the method of testing being to place a number of the pyramids, having melting-points near to that of the furnace temperature, on an earthenware support, and insert them in the furnace. The effect is shown in Fig. 50; one of the pyramids has completely melted and fallen flat; the next has bent over; whilst the other two are intact. The temperature of the furnace is taken as that of the melting-point of the pyramid which has bent over, but not collapsed, and which may be obtained from the number stamped on it. The most refractory pyramids are composed of alumina and silica in varying proportions, other ingredients, such as potash, lime, etc., being introduced to obtain the more readily fusible pyramids.

Sege*r* pyramids are largely used by pottery manufacturers, and are commercially known as "fusible cones." They possess advan-

tages over other fusion methods not only in respect to the range covered, but also in accuracy owing to the nearness of the melting-points of consecutive pyramids. They may be used to indicate the rise in the temperature of a furnace by observing the bending over in

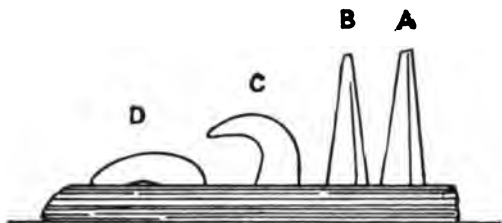


FIG. 50.—METHOD OF USING SEGER "CONES."

turn of a number inserted in the furnace. It may be added that a number of pyramids, suited to a given operation, may be purchased at a trifling cost.

Cylinders of fusible materials, which melt completely at specified temperatures, have been introduced for use in steel furnaces under the name of "Sentinel" pyrometers.

Other Forms of Pyrometers.—In addition to the forms already described, numerous other pyrometers have been devised from time to time. Amongst these may be mentioned (*a*) the mercury vapour pyrometer, in which mercury is enclosed in a steel tube to which a pressure-gauge is attached, and the temperature deduced from the observed pressure of the mercury vapour; (*b*) pyrometers based on the rise in temperature observed in a steady stream of water or air driven through a tube placed in the furnace; (*c*) pyrometers in which the temperature is obtained from the variations in the viscosity of gases with temperature, or from the alteration of the refractive index; (*d*) instruments depending upon the observed pressure of a gas or vapour liberated on heating a weighed quantity of solid; and many others. None of these are in such general use as to demand a detailed description in the limits of the present treatise.

High Temperature Data.—The following table may be of interest as showing the progress made in connection with the measurement of very high temperatures.

Source	Temperature, °C.	Observer and Method
Incandescent electric lamp (carbon) }	1800	Le Chatelier, optical pyrometer
Arc lamp	4100	" " "
Arc lamp	3760	Féry, heat radiation pyrometer
Thermit in mould . . .	2500	" " "
Bunsen flame, open . . .	1870	Féry, spectroscopic method
" closed	1710	" " "
Acetylene flame	2550	" " "
Oxy-hydrogen flame . . .	2420	" " "
Melting point of tantalum . .	3000	{ Waidner and Burgess, optical pyrometer
" " tungsten	3200	{ Waidner and Burgess, optical pyrometer
Temperature of sun	7600	Le Chatelier, optical pyrometer
" "	7500	Féry, heat-radiation pyrometer

Recent Developments of Pyrometry.—Owing to readings on the gas scale now being possible up to 1550° C. (p. 135), the uncertainty of the indications of instruments between 1000° C. and the above temperature has now been removed. Improvements in resistance pyrometers have been made by Paul and Northrup, who have introduced indicators practically automatic in action. Cheap thermo-electric pyrometers have been placed on the market by various firms for temperatures up to 1000° C., the couples used being iron and constantan, nickel and copper, and nickel and carbon; and the author has devised a method of automatic compensation for fluctuations in the temperature of the cold junction. Radiation pyrometers have been added to by the Cambridge Scientific Instrument Company, who have introduced a form of Féry pyrometer in which the thermal junction is replaced by a compound strip in spiral form, which coils up or uncoils with changes of temperature, and carries a pointer moving over a scale which is marked so as to give direct readings of the temperature of the source. A radiation pyrometer which, within moderate limits, requires no focusing, has been devised by Foster. Holborn's optical pyrometer (p. 176) is now made in commercial form by Messrs. Siemens, and has found a use in the treatment of special steels at very high temperatures.

CHAPTER IX.

CHANGE OF STATE. FUSION.

Physical Effects of Heat on Solids.—When the temperature of a solid is raised, the kinetic energy possessed by its molecules is augmented, and the freedom of motion of the molecules increases. Cooling produces the converse effect, and consequently, at different temperatures, the physical properties of solids might be expected to differ, and this is generally true. Indiarubber, for example, becomes hard in cold weather, and, if dipped in liquid air becomes so brittle that it may be broken up with a hammer. In the case of metals a molecular rearrangement often results from heating, which may remain permanent on cooling. Thus metals which have been rendered hard by rolling or drawing into wire are often permanently softened by heating, as may be noticed in the case of brass and copper. The annealing of metals is explained in this way, and a microscopic examination of the etched surface of the metal shows a different structure after annealing than before. An interesting example of the molecular changes caused by a rise of temperature is furnished by zinc, which, if cast, is brittle at ordinary temperatures. On heating to 100° – 150° C., however, the metal becomes malleable, and may be drawn into wire; but at 300° C. it again becomes extremely brittle. Bismuth, which ordinarily possesses little tensile strength, improves greatly in this respect at very low temperatures, and steel which has been dipped in liquid air shows a permanent increase in tensile strength.

The electrical resistance of various substances is also modified by changes of temperature. Pure metals have in general a high temperature coefficient; that is, show a rapid increase in resistance as the temperature rises and a correspondingly rapid decrease as the temperature falls. Alloys, in general, have a lower temperature coefficient, and in special alloys such as German silver, platinoid, and constantan, the resistance only alters very slightly with the temperature. Certain other substances, such as porcelain, are practically non-conductors of electricity when cold, but at high temperatures

conduct freely. Such bodies are known as pyro-conductors, the conducting power being due to molecular alterations caused by the rise in temperature. The Nernst lamp consists of a filament of pyro-conducting material, which after a preliminary heating conducts the current, and offers sufficient resistance to remain luminous when a current through it is once established.

Critical Points of Steel.—The molecular changes occasioned in steel by alterations of temperature call for special mention, as a study of these changes may often prove a valuable guide to the successful treatment of the metal. The phenomenon of recalescence has already been mentioned (see Chapter IV.), and the temperatures at which recalescence occurs—known as the “critical points”—vary with the class of steel, and may be used to furnish a clue to the character of the steel under test. It being known by experience how to treat steels of different kinds for the purposes intended, the determination of the critical points becomes a matter of commercial utility.

One method of determining these points is to place a platinum-resistance or thermal-couple pyrometer in a hole drilled in the specimen, the temperature being raised slowly by a gas furnace, or better still, an electric furnace. The molecular change with rising temperature is accompanied by an absorption of heat, so that at the critical points the temperature for a short time will cease to rise. If readings be taken every half-minute, and a curve connecting time and temperature be drawn, it will show a flexure when the critical point is reached. The curve will be traced automatically if a recorder is used with the pyrometer. On cooling the steel, evolution of heat occurs at the recalescent points, and flexures would again be observed if a curve were traced as before. Such a cooling curve is shown in Fig. 51.

A second method, more sensitive than the foregoing, is known as the “differential” method. A block of metal known to be free from molecular changes of this kind is placed side by side in the furnace with the specimen of steel, as indicated in Fig. 52, so that both blocks would show the same rise in temperature in the absence of a molecular change. In a hole drilled in the specimen A, a thermal-junction C is placed, connected to a galvanometer G, the scale of which has been graduated to read temperatures. The second galvanometer H is in circuit with two junctions, D and E, one in the specimen and the other in the comparison piece B. So long as the junctions D and E remain at the same temperature, no deflection will be observed on the galvanometer H, any tendency to send a current on the part of either being counterbalanced by an equal tendency on the part of

the other to send a current in the opposite direction. If the temperature of the furnace be raised slowly, no movement on H will be noted until a molecular change occurs in the specimen A, which, by

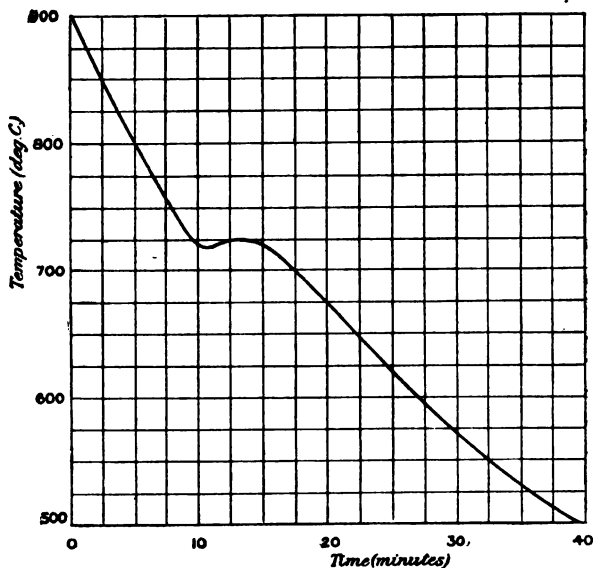


FIG. 51.—COOLING CURVE FOR STEEL, SHOWING RECALESCENCE.

absorbing heat, causes the temperature to lag behind that of B. The temperature at which the galvanometer H commences to deflect is

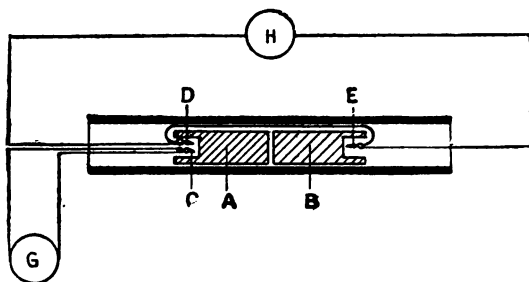


FIG. 52.—DIFFERENTIAL METHOD OF DETERMINING RECALESCENCE POINTS OF STEEL.

recorded on G, and the critical point thus determined. The temperature may now be raised some 50° above this point, and then allowed

to fall gradually, when a deflection on H, but in the opposite direction, will again be obtained at the critical point, as owing to recalescence A remains at a higher temperature than B. In performing the experiment, an electric furnace is suitable, and all the junctions should be naked. The wires should be threaded through twin-bore fireclay tubes, which rest in the holes in A and B, and prevent contact with the mass of metal. The specimen and comparison-piece should rest on mica in the porcelain or silica tube of the furnace. This method is very sensitive and well adapted for testing steels which do not show a marked recalescence. Any undue rise in temperature on the part of either piece of metal, due to a more favourable position in the furnace, would be detected in the early stages by a movement of H.

The molecular changes which occur when steel is heated are only partially reversed when the steel is rapidly quenched. Hence, a piece of hot steel, when cooled rapidly in water or oil, retains to a large extent the molecular structure possessed at the higher temperature, and differs from slowly-cooled steel in being harder and more brittle. Tempered steel is intermediate between the hard and slowly-cooled or soft steel both in structure and properties. The modifications caused by the introduction of metals such as tungsten, chromium, etc., cannot be dealt with here, but it may be stated that a knowledge of the critical points, in the hands of a competent metallurgist, is of great service in guiding the operations carried out in working the steel.

Change of State.—When the temperature of a solid is continuously raised, a point is reached at which fusion occurs, and the solid becomes a liquid. The temperature at which fusion takes place is called the “melting-point” of the solid; and the temperature at which the substance, on cooling, re-assumes the solid state is known as the “freezing” or “setting point.” In most cases these two temperatures are identical, but when the transition is not abrupt a difference of several degrees may exist between the temperature at which the substance ceases to be a well-defined solid, and that at which it flows freely. Many solids, before liquefying, pass through an intermediate or pasty state, in which the properties are midway between those of a solid and a liquid, as may be observed with cast-iron and other metals. It is advisable, therefore, in all observations on the change of state, to distinguish between the temperatures which bound this intermediate condition.

The liquefaction of a solid is always accompanied by an absorption of heat, which is converted into work in conferring increased velocities on the molecules, and therefore cannot be detected by a

thermometer. When the liquid solidifies, the heat absorbed in the act of liquefaction is liberated. The term "latent heat of fusion" is applied to the heat energy necessary to change the solid, already at its melting-point, into liquid also at the melting-point; or to that liberated in the converse change. It is owing to the absorption of this latent heat that a block of ice placed in a room, and continuously receiving heat from the atmosphere and surrounding objects, remains at 0°C . until completely melted; moreover, the water resulting from the melting has also a temperature of 0°C . Hence all the heat received by the ice has been converted into another form of energy, having been utilised in imparting the greater kinetic energy possessed by the molecules in the liquid state. The liberation of latent heat is noticed when a liquid is cooled until solidification occurs. A thermometer placed in the liquid shows a continuous fall of temperature until the freezing point is reached, when, owing to the disengagement of the latent heat, the temperature remains steady for some time, falling again when solidification is complete. If a small beaker be filled with paraffin wax, and a thermometer be placed in the centre of the mass after melting, it will show a continuous fall of temperature until 49°C . is reached. At this temperature it will remain for 15 minutes or more, depending on the size of the beaker and the rate of cooling. The observation of the stationary temperature is used to determine the freezing point of solids.

Determination of the Melting-Point of Solids. First Method, for solids which melt below 300°C .—A narrow piece of thin-walled glass tubing, closed at one end, is fastened to a thermometer by means of a piece of wire or a rubber ring. A small piece of the solid is placed in the tube, and pushed down with a wire until it is opposite the centre of the thermometer bulb. The tube and thermometer are then immersed in a bath of strong sulphuric acid to a sufficient depth to cover the part of the tube occupied by the solid; the open end of the tube, however, or the rubber ring, must not be submerged. The bath is gradually heated with a Bunsen burner, until the solid is observed to liquefy and trickle down the tube. The reading of the thermometer is then taken, and gives the melting-point of the solid. To obtain an exact reading, the bath should be continuously stirred, and the temperature raised very gradually as the melting-point is approached. A quickly performed experiment indicates the melting-point to within a few degrees, and a second may then be performed in which the final stage is conducted very slowly.

Second Method, generally applicable.—A thin-walled iron or platinum tube, $\frac{1}{8}$ inch in diameter, and 4 inches long, closed at one

end, is filled with the solid and heated until liquefaction occurs. An iron or platinum spiral is placed in the molten mass, so as not to touch the tube, and the mass is now allowed to solidify, thus fixing the wire in the centre of the solid. The tube is now placed in a suitable bath, and fixed in position by means of a stand; and a thermometer or pyrometer is placed side by side with the tube. The free end of the wire is passed over a pulley, and a 50-gram weight attached to it. The temperature of the bath is gradually raised until the portions of the solid in contact with the walls of the tube become liquid, when the weight will be observed to fall and drag out the solid core. The temperature of the bath at this moment gives the melting-point, provided that the last stages of the heating have been conducted very gradually.

For melting-points not exceeding 300°C ., a bath of strong sulphuric acid may be used. Above this temperature molten tin may be used in conjunction with an iron tube, or suitable fused salts with a platinum tube. Platinum should never be used when the bath or substance tested is metallic in character, or contains free caustic alkalies. A platinum-resistance pyrometer may be used for melting-points not exceeding 1200°C .; above this temperature a thermoelectric pyrometer is necessary.

Determination of the Freezing-Point of Solids.—A quantity of the solid is melted in a crucible or other suitable vessel, and raised to 30° or 40° above its melting-point. A thermometer or pyrometer—according to the temperature—is placed in the molten mass, and its indications observed as the liquid cools. When solidification occurs, the liberation of latent heat suffices to maintain a steady temperature for some time, after which continuous cooling will again take place. The stationary temperature is taken as the freezing-point of the solid.

The time during which the temperature is steady depends upon the rate of cooling, the mass of substance used, and the quantity of latent heat disengaged. So long as the latent heat liberated balances the cooling due to radiation and other causes, the temperature will not alter. Hence at high temperatures, when the rate of cooling due to radiation, etc., is rapid, a large mass of substance is necessary if the stationary temperature is to continue for any length of time; or the same result may be secured by allowing a smaller quantity of the substance to cool in the interior of the furnace in which it was melted. The definite character of the freezing-point, as thus observed, renders the method suitable for the graduation of pyrometers by the use of standard substances of known freezing-points.

The results may with advantage be recorded graphically, the temperature being noted every half-minute, and a curve drawn on squared paper connecting time with temperature. The general form of curve obtained with a single substance is shown in Fig. 53. At the solidification temperature the curve becomes parallel to the time axis, to which, at other temperatures, it is inclined. When the cooling

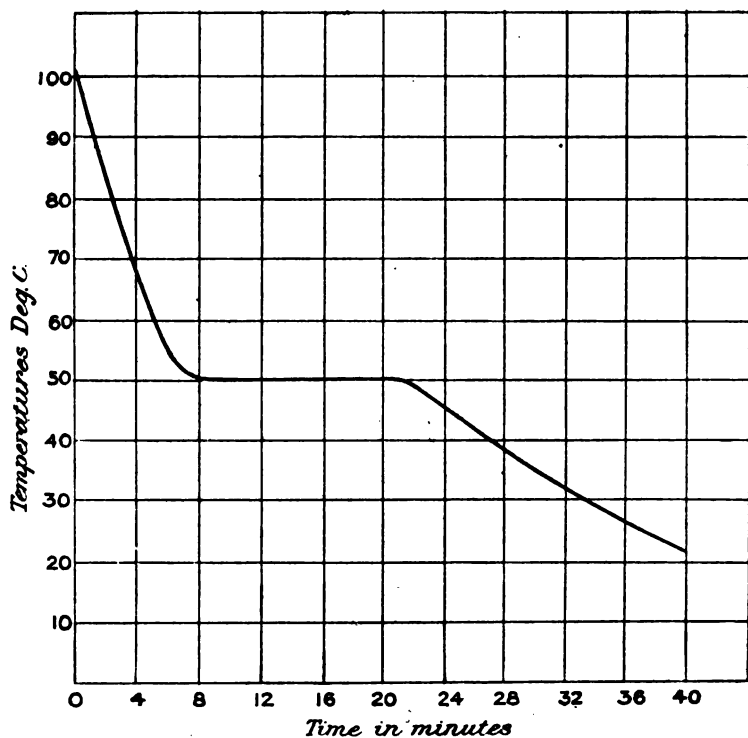


FIG. 53.—COOLING CURVE FOR A PURE SUBSTANCE PASSING FROM LIQUID TO SOLID.

has been too rapid for stationary readings to be observed, a flexure of the curve is obtained at the solidification point, sufficient to give a clue to the temperature.

In determining the freezing-point by this method, it may frequently be noticed that the substance cools continuously for a time, and then undergoes a sudden rise in temperature, at which it remains steady until solidification is complete. This failure to set until the tempera-

ture has fallen below the normal setting or freezing-point, is known as "surfusion," and will be specially referred to later. When solidification occurs, however, the temperature rises at once to the true freezing-point, and remains stationary as before; hence, in all cases the steady temperature gives the correct freezing-point.

The melting-points of metals are in general identical with the freezing-points, and consequently the method under notice will furnish the melting-points of these substances; for which purpose it is to be preferred to either of the methods previously described. The special case of alloys will now be considered.

"Partial" Melting-Points of Alloys. Eutectics.—Alloys of metals differ in physical properties from those of the constituents in a marked manner, and are not merely simple mixtures of the component metals. In the simplest case an alloy may be a true chemical compound, with a uniform structure, and will then possess a definite melting-point. In a more complicated case, such a compound may be diffused through the mass of another metal, and the alloy will then possess "partial" melting or freezing points, one for the compound, and the other for the metal; or a number of partial melting-points may be observed if the constitution of the alloy is still more complex. The constituent which possesses the lowest melting-point is called the "eutectic," and, in a given alloy, has a definite composition. In the act of solidification, therefore, the constituent of the higher melting-point settles out first, leaving the eutectic still liquid, the action being comparable to the crystallisation of a salt from the mother-liquor. Hence a cooling-curve for an alloy which is not a homogeneous chemical compound, will show two or more flexures or straight parts, corresponding to the setting of the constituents in turn, each of which liberates latent heat in the act of solidification. The structure of an alloy will therefore consist of a matrix formed by the eutectic, which is the last to solidify, interspersed by the other ingredients. Each partial setting corresponds to the separation of a substance from the molten mass, and hence the number of distinct components may be deduced from the number of the partial setting-points observed.

It must not be supposed that because a given alloy of two metals has two partial freezing-points that these correspond to the separate solidification of the pure metals. On the contrary, the first setting generally represents the solidification of an alloy of the two metals of a definite composition, and the second, that of the eutectic, which also contains both metals, but in a different proportion; and the temperatures at which solidification occurs is in neither case identical with that of either component metal. The whole question of the structure

of alloys and its relation to the freezing-points is dealt with at length in the reports of the Alloys Research Committee in the Proceedings of the Institution of Mechanical Engineers, to which the reader is referred for detailed information.

Melting-Points of Mixtures.—The melting-point of a substance is generally lowered by the presence of another substance, a small quantity of which may suffice to cause a notable fall in the melting-point. Thus pure iron, which melts just above 1500°C. , has its melting-point reduced by more than 300° when less than 1 per cent. of carbon is present. A mixture of equal parts of common salt and potassium chloride melts at a lower temperature than either of the constituents, and the same holds true for a mixture of sodium and potassium carbonates. In general, the melting-point of a mixture is always lower than that of the constituent which has the higher melting point, and frequently lower than that of either.

TABLE OF MELTING-POINTS OF MIXTURES OF LEAD AND TIN.

Composition: Parts by Weight		Melting-Point	
Lead	Tin	Degrees C.	Degrees F.
1	0 (Pb)	327	620
7	1 (Pb ₇ Sn)	292	558
5½	1 (Pb _{5½} Sn)	283	541
3½	1 (Pb _{3½} Sn)	270	518
1½	1 (PbSn)	235	455
7	8 (PbSn ₈)	197	387
10	17 (PbSn ₁₇)	181	358
10	19 (PbSn ₁₉)	180	356
1	2½ (PbSn _{2½})	186	367
10	28½ (PbSn _{28½})	194	381
0	1 (Sn)	232	450

As the amount of impurity in a substance increases, the melting-point usually falls until a minimum is reached, after which further additions of the second substance cause a progressive rise in the melting-point. The mixture which possesses the minimum melting-point is known as the eutectic mixture of the two substances. The eutectic for iron and carbon has the composition—iron, 99·11 per cent., and carbon, 0·89 per cent. Mixtures of lead and tin furnish

an interesting example of the lowering of melting-point, and an inspection of the table on page 190 shows that the eutectic mixture of these two metals melts at 180°C ., and is composed of 10 parts by weight of lead to 19 parts by weight of tin, or in the proportion of 1 atom of lead to 3.3 atoms of tin.

The temperatures given above are to be regarded as the melting-points of the constituent which first settles out as the liquid is cooled ; the lower constituent, whatever the composition, solidifies at approximately 180° , and is the eutectic $\text{PbSn}_{3.3}$. When the alloy possesses this composition, only one setting point is observed, and the whole mass consists of the eutectic. Any variation from this composition causes a constituent of higher melting-point to separate out before the eutectic has solidified.

Alloys of very low Melting-Point, or Fusible Alloys.—By alloying several metals it is possible to obtain a product which possesses an extremely low melting-point—considerably less than the temperature of boiling water. Many of these “fusible alloys” are known, and the composition and melting-point of several are appended :—

TABLE OF ALLOYS OF VERY LOW MELTING-POINT.

Composition : Parts by Weight				Melting-Point	
Tin	Bismuth	Lead	Cadmium	Degrees C.	Degrees F.
25	50	10	..	120	248
8	25	10	..	100	212
6	40	10	..	95	203
1	4	2	1	65	149
4	15	8	3	60	140

By varying the above quantities alloys may be produced which possess any desired melting-point between the upper and lower limits. Fusible alloys have some important practical applications, which will be considered in the succeeding chapter.

Change of Volume on Melting.—In most cases the melting of a solid is accompanied by an increase in volume, that is, the liquid occupies a greater bulk than the solid from which it was derived. Conversely, on solidifying, a decrease in volume is generally observed. The density of the solid in such cases is, therefore, greater than that of the liquid, and consequently a piece of the solid will sink if dropped into the liquid. Exceptions to this rule are found in the cases of

water, bismuth, antimony and grey cast-iron ; all of which expand in the act of solidification. One cubic foot of water at 0°C . becomes 1.09 cubic feet of ice at 0°C .—hence ice will float on water, being less dense. The force exerted in the act of expanding at the moment of solidification is great, and if the water be confined may suffice to burst the enclosure. The bursting of water-pipes and the breaking up of porous rocks in frosty weather are due to the expansive force thus exerted ; the result, however, is not made evident until a thaw occurs. The expansion on solidification which takes place with grey cast-iron, antimony and bismuth, is manifested by the sharp definition of castings obtained from them, as in solidifying the metal is squeezed into the finest lines of the mould. Antimony and bismuth are mainly used for alloys, to which they impart the property of expanding on setting. Most metals and alloys contract on solidifying, and castings obtained from them are not so sharply defined. Waxes, fats, and organic substances generally, as well as salts, show a contraction on entering into the solid condition.

The finished size of a metal casting will differ from that of the pattern used for making the mould, partly because of the alteration in volume on setting, and partly because of the contraction of the solid in cooling down to the atmospheric temperature. Other factors are the expansion of the mould, and the temperature at which the metal is poured. A table is given on page 77 which shows the allowance to be made in a pattern for various metals, in order to produce castings of a given size.

Effect of Pressure on the Melting-Point.—If a solid, just about to melt, be subjected to pressure, the tendency to increase in volume on liquefying will be opposed ; whilst a tendency to contract on liquefying will be assisted. Hence it might be inferred that pressure, in the case of ordinary solids, will retard melting, and thus raise the melting-point, whilst in the case of ice, bismuth, etc., the process will be accelerated, and consequently the melting-point will be lowered. These conclusions may be verified by experiment. Thus Bunsen found that a sample of wax, which melted at 46.3°C . under 1 atmosphere, fused at 49.9°C . under a pressure of 100 atmospheres. Prof. James Thomson showed that when the increase or decrease in volume accompanying the change of state was known, the alteration in melting-point due to a given pressure could be calculated from thermodynamic principles, and thus found that 1 atmosphere additional pressure should lower the melting-point of ice by $.0075^{\circ}\text{C}$. The experimental verification of this result was made by Lord Kelvin, who obtained a figure closely agreeing with the calculated

TABLE OF MELTING-POINTS.

Substance	Melting-Point, Degrees C.	Melting-Point, Degrees F.
<i>Metals—</i>		
Tungsten	3200 (about)	5900 (about)
Tantalum	3000 "	5400 "
Platinum (Harker)	1710	3110
" (Burgess)	1753	3187
Pure iron	1510	2750
Palladium	1500	2732
Nickel	1427	2600
Copper (in reducing atmosphere)	1084	1983
" (in air)	1064	1947
Gold	1064	1947
Silver (free from oxygen)	962	1763
" (in air)	955	1751
Aluminium	657	1214
Antimony	632	1169
Zinc	419	786
Lead	327	620
Cadmium	321	610
Bismuth	268	514
Tin	232	449
Mercury	- 39	- 38
<i>Non-Metallic Elements—</i>		
Sulphur (rhombic)	114	237·2
Phosphorus (yellow)	43·3	110
Bromine	- 7	19·4
Chlorine	- 34	- 29
Nitrogen	- 214	- 353
Oxygen	- 238	- 396
Hydrogen	- 257	- 431
<i>Pure Salts—</i>		
Saltpetre	399	750
Potassium chloride	735	1355
Common salt	800	1472
Sodium sulphate (dry)	900	1652
Potassium sulphate (dry)	1070	1958
Magnesium sulphate (dry)	1150	2102
Calcium silicate	1700	3092
<i>Other Substances—</i>		
Glass (soft)	1100	2012
Paraffin wax	54-66	129-115
Ammonia	- 75·5	- 104
Alcohol	- 112	- 170
Ether	- 113	- 171
Nitrous oxide	- 150	- 238
Water	0	32

result. Later work by Prof. Dewar indicates that an additional 140 atmospheres cause the melting-point of ice to fall by $1^{\circ}\text{C}.$; an average lowering of $.0072^{\circ}\text{C}.$ per atmosphere.

As a result of the effect of pressure on the melting-point, it is surmised that the internal portions of the earth, although possessing a temperature much higher than the normal melting-point of the materials, is kept in a solid or semi-solid state owing to the enormous pressure of the overlying rocks. The anomalous behaviour of ice in respect to the increase of pressure explains many curious phenomena that may be observed. Thus, as Bottomley showed, if a wire be placed across a bar of ice, and a weight be suspended from each end, the weighted wire will pass through the ice, but will not leave it in two separate pieces. The effect of the pressure on the ice beneath the wire is to cause it to melt, but the water produced escapes round the wire and freezes again, and this occurs until the wire has passed through the bar. The adhesion of snow under compression, as in making a snowball, is similarly explained; the pressure causes a partial melting of the particles of snow, and on liberating the pressure the water produced freezes and binds the particles together. Similarly, two pieces of ice, if pressed together, will adhere or join together to form a single piece. This property of joining under pressure is known as "regelation," and was first called attention to by Faraday.

Melting-Points of Various Substances.—The table on page 193 gives the melting-points of a number of solids at ordinary pressures. Decimals are in most cases omitted.

The figures given in the table represent the most recent determinations. Exact information as to the melting-points of pure salts is scanty, and further investigations in this direction are desirable with a view to establishing cheap standards for graduating pyrometers. The very low temperature data represent the observations of Professor Dewar.

Surfusion, or Delayed Solidification.—The fact that water, if free from suspended matter, may be lowered considerably below the freezing point and yet remain liquid, was noticed by Fahrenheit in 1724. This phenomenon has since been observed with many other substances such as phosphorus, sulphur, tin, antimony, and fused salts, and is termed "surfusion." If a surfused liquid be shaken, it will frequently solidify, and in all cases the insertion of a fragment of the solid will cause solidification. The disengagement of latent heat on setting raises the temperature to the melting-point; obviously the temperature cannot exceed this, as some of the solid would be re-

melted, and the latent heat re-absorbed. The converse phenomenon of delayed melting may also be observed in certain cases, where the temperature must be raised above the normal melting-point before liquefaction commences.

A surfused liquid, if continuously cooled, will ultimately solidify without shaking or dropping in a piece of the solid. A mass of molten antimony, for example, may be noticed to cool down to $600^{\circ}\text{C}.$,

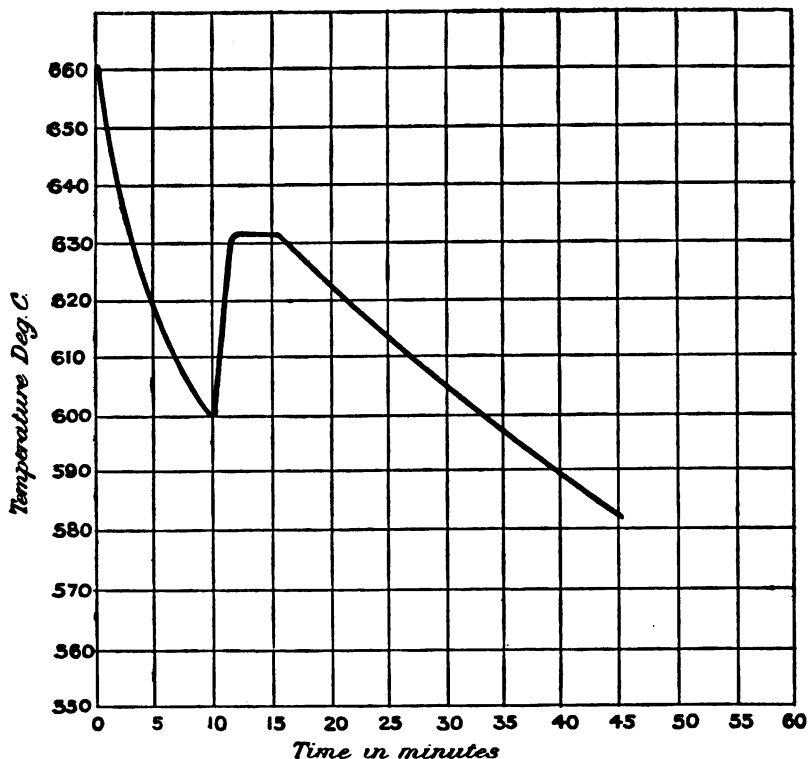


FIG. 54.—COOLING CURVE FOR ANTIMONY, SHOWING SURFUSION.

showing 32° of surfusion; it then sets spontaneously and the temperature rises to the melting-point, $632^{\circ}\text{C}.$ A cooling curve under these circumstances takes the form shown in Fig. 54. Water in the surfused condition in a Bunsen calorimeter may always be made to freeze by placing solid carbon dioxide in the inner tube.

The supersaturation of solutions in some respects resembles the

phenomenon of surfusion. If water be made to dissolve as much as possible of a salt when boiling, and the solution be kept still and free from dust on cooling, the crystals which usually deposit, owing to less solubility at lower temperatures, remain in solution. Shaking, or dropping in a crystal of the solid, will cause crystallisation to occur, with considerable generation of heat. So small is the crystal required to initiate the deposition, that a knitting-needle dipped in a mass of crystals, and afterwards cleaned with emery paper, will often retain sufficient of the solid to cause crystallisation when the needle is placed in the solution.

The phenomena of surfusion and supersaturation are due to the molecules having attained a state of unstable equilibrium, which a slight disturbance of the right kind serves to upset. An analogy may be drawn from a row of bricks placed on end within reach of one another, when knocking over the end brick causes the whole row to fall.

Latent Heat of Fusion.—Reference has already been made to the absorption of heat by a substance on melting, which is restored on solidification. The numerical value of the heat quantity involved is defined as follows:—*The latent heat of fusion of a substance is the number of calories absorbed by 1 gram on being converted from the solid to the liquid state, without change of temperature.* Thus by saying that the latent heat of fusion of ice is 80 calories per gram, is meant that one gram of ice at 0°C. , on becoming water at 0°C. , absorbs 80 calories. Black found the value for ice by trial with different quantities of water and ice, which he mixed and noted the result. He ultimately found that when 1 lb. of water at 79.4°C. (or its equivalent in degrees F.) was mixed with 1 lb. of ice at 0°C. , the temperature of the whole after mixing was 0°C. , and all the ice was melted. With a less quantity of ice the temperature of the mixture did not fall to 0°C. , with a greater quantity some remained unmelted. Hence 1 lb. of ice on melting to water at the same temperature absorbed $79.4\text{ lb.}^{\circ}\text{C.}$ units of heat. More exact methods indicate 80 calories per gram, or $80\text{ lb.}^{\circ}\text{C.}$ units per pound, as the correct value for the latent heat of fusion of ice.

The value of the latent heat of fusion of ice may be determined by adding dried ice (prepared by squeezing between blotting-paper) to a known quantity of water at a known temperature, and noting the temperature of the mixture after the ice has melted. The increase in weight of the water gives the amount of ice added, and the latent heat of fusion is calculated by equating the heat lost by the water and vessel to that gained by the ice.

Example.—A calorimeter weighs 100 grams, and is made of material of specific heat 0.1. It contains 520 grams of water at 19.8° C., and on adding a quantity of ice temperature falls to 10.5° C. The weight of ice added, as determined by weighing the calorimeter and its contents, is 55 grams. Then from the equation—

$$\text{Calories gained by ice} = \begin{cases} \text{calories lost by water} \\ \text{and calorimeter} \end{cases}$$

we have

$$(L \times 55) + (55 \times 10.5) = 520 \times (19.8 - 10.5) + \{(100 \times 0.1) \times (19.8 - 10.5)\}$$

$$\text{and } L = 79 \text{ calories per gram.}$$

It should be noted that the calories gained by the ice represent (a) the heat required to melt it, producing water at 0° C., which is the latent heat; and (b) the heat required to raise the water formed from 0° C. to that of the mixture.

The drawback of this method is the difficulty of obtaining perfectly dry ice. When wet, a low result will be obtained, and more accurate results are furnished by the use of a Bunsen calorimeter. If 10 grams of water at 10° C. be placed in the tube of this calorimeter, 100 calories will be given out on cooling to 0° C. The amount of ice melted by this quantity of heat is found from the observed contraction, and hence the calories required to melt 1 gram of ice are readily calculated.

It is more difficult to find the value of the latent heat of fusion of other solids by this method, as the specific heat of the substance both in the liquid and solid state must be known. A table of latent heats of fusion is appended, the values being given both in heat and work units.

An inspection of the table on page 198 shows that the latent heat of fusion of ice is much greater than that of any of the other substances enumerated. The value of ice as a cooling agent is thus greater than that of any other solid which might be used; hence for cooling purposes ice is not only cheapest, but best. The value for metals varies considerably; thus the melting of grey cast-iron involves an absorption of heat five times as great as that required for an equal weight of nickel.

The amount of energy absorbed in the process of melting is best judged by a consideration of the work equivalent of the latent heat. In the case of ice, the energy absorbed by 1 lb. on becoming water at 0° C. would suffice to raise a weight of 1 ton through a height of

TABLE OF LATENT HEATS OF FUSION.

Substance	Latent Heat of Fusion			
	Calories per gram	B.Th.U. per lb.	Ergs per gram	Ft.-lb. per lb.
<i>Metals—</i>				
Bismuth . . .	12·6	22·7	52·9 × 10 ⁷	17,640
Cadmium . . .	13·7	24·7	57·5 „	19,180
Cast iron (grey) . .	23·0	41·4	96·6 „	32,200
„ (white) . .	33·0	59·4	138·6 „	46,200
Lead . . .	5·4	9·7	22·7 „	7,560
Mercury . . .	2·8	5·04	11·8 „	3,920
Nickel . . .	4·6	8·3	19·3 „	6,440
Platinum . . .	27·2	49·0	114·2 „	38,080
Silver . . .	21·1	38·0	88·6 „	29,540
Tin . . .	14·3	25·7	69·1 „	20,020
Zinc . . .	28·1	50·6	118·2 „	39,340
<i>Other Substances—</i>				
Ice . . .	80·0	144·0	336·0 „	112,000
Bromine . . .	16·2	29·2	68·0 „	22,680
Phosphorus (yellow) .	5·2	9·4	21·8 „	7,280
Sulphur (rhombic) .	9·4	16·9	39·5 „	13,160
Hydrogen . . .	16·0	28·8	67·2 „	22,400

50 feet, or is equal to 50 foot-tons. The energy possessed by the molecules of 1 lb. of water at 0° C. therefore exceeds that contained by 1 lb. of ice by 50 foot-tons.

Effect of Dissolved Solids on the Freezing-Point.—The freezing point of liquids in general is lowered by the presence of dissolved solids, the depression being, within limits, proportional to the amount of solids dissolved. Strong solutions of salt or calcium chloride may be cooled to -20° C. or lower without freezing, and for this reason are used to circulate at a low temperature in cold stores. Sea water, for the same reason, does not freeze so readily as fresh water. It has been found that if quantities of different salts be dissolved in equal quantities of a given liquid, in the proportion of the molecular weights of the salts, the various solutions will possess the same freezing-point. Thus a solution of 40 grams of caustic soda in

1000 grams of water, will freeze at the same temperature as a solution of 101 grams of saltpetre in 1000 grams of water, the molecular weights of the salts taken being 40 and 101. In the case of non-electrolytes, such as sugar, the depression in freezing-point is only one-half that occasioned by the molecular equivalent of salts. These observations have been applied to the determination of molecular weights.

CHAPTER X.

PRACTICAL APPLICATIONS OF FUSION AND ALLIED PHENOMENA.

Welding.—Two pieces of iron may be made to unite perfectly by the operation known as welding. The surfaces to be united are raised to the fusion point, and placed together, a little sand or borax having first been thrown on each to form a flux with any oxide that may have formed. The adhering surfaces are then well hammered, and the iron remains in a pasty condition for a sufficient time to allow the two metallic surfaces to be thoroughly incorporated with each other. A good welded joint should be as strong as any other part of the pieces joined. The ends of the separate links of iron chains are joined together by welding, and the operation is a very common one in the work of a blacksmith. The welding of steel may also be accomplished, but demands greater care and a more exact judgment of the correct temperature. Only those metals can be welded which remain in the pasty state for a considerable time—a property possessed by iron, steel and platinum. Others, such as copper, solidify too abruptly for the process to succeed.

Soldering.—The common method of uniting two metallic surfaces by the aid of a metal or alloy, known as soldering, is usually carried out by the use of an alloy of lead and tin, called “solder.” Coarse solder contains 2 parts by weight of lead to 1 part of tin, and flows at $240^{\circ}\text{C}.$; common solder consists of equal parts of lead and tin, melting at $200^{\circ}\text{C}.$; whilst fine solder is composed of 2 of tin to 1 of lead, and fuses at $180^{\circ}\text{C}.$ These alloys possess a lower melting-point than the metals they are used to unite, and if the surfaces be clean, and sufficiently hot, the alloy adheres to both, forming a perfect joint. For cleaning the surfaces, zinc chloride or “killed spirit” is used for ordinary work; and resin for electrical work, such as joining cables and wires. In making a large “wiped” joint, as on water pipes, a large mass of solder is placed on the joint, and heated to its melting-point. It remains plastic for a sufficient time to enable the plumber to work it into any desired shape by means of a piece of leather held in the hand.

Automatic Water-Sprinklers.—The production of alloys which melt at low temperatures is utilised in the construction of automatic water-sprinklers, in which a water supply is held in check by means of a fusible alloy. When the temperature rises to a dangerous point, owing to an outbreak of fire, the fusible alloy melts, and allows water to be sprinkled into the room ; thus enabling a fire to be extinguished in the early stages. These appliances are now extensively used in cotton mills, cabinet-making factories, and other places where inflammable materials are kept, and have undoubtedly been successful in preventing many serious fires. Many forms of water sprinklers are in use, and several typical examples will now be described.

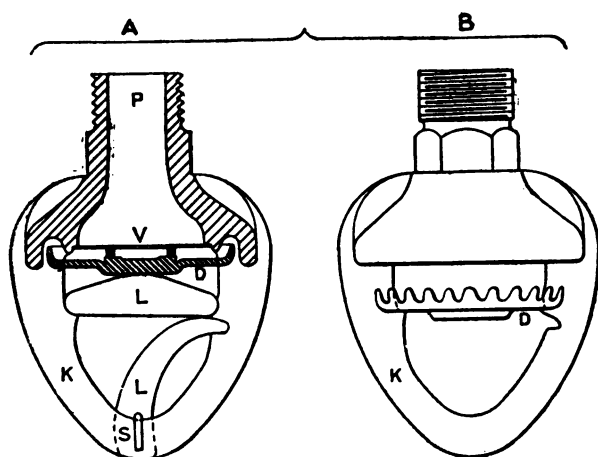


FIG. 55.—GRINNELL'S SPRINKLER : A, CLOSED ; B, OPEN.

Grinnell's sprinkler (Fig. 55) consists of a pipe P, connected to the water supply, and closed at the lower end by the valve V, which rests on the splash-plate D. The valve is kept closed by the levers L L, of which the lower one is fastened to the yoke K, by means of fusible alloy at S. When the surrounding temperature rises to the melting-point of the alloy, the levers give way, and the pressure of the water opens the valve. The splash-plate D falls to a lower position, and its serrated edge causes water falling upon it to be scattered in all directions. The illustration shows the sprinkler before and after the melting of the alloy. A more recent form of Grinnell sprinkler is shown in Fig. 56, the valve in this case con-

sisting of a hemisphere of glass V, on the convexity of which is placed a covering of Babbitt metal. A flexible diaphragm is pressed against V by the water pressure in P, and a water-tight joint is thus secured.

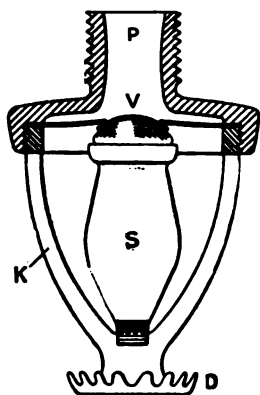


FIG. 56.—GRINNELL'S SPRINKLER (Later form.)

The valve is held in position by the strut S, formed of several pieces of metal soldered together with fusible alloy, and resting on the yoke K, which also carries the splash-plate D. This arrangement is simpler than the earlier form, and easier to restore after having been in operation.

In Walworth's sprinkler, Fig. 57, the soldered part consists of a link only, and not only is such an arrangement prompt in action, but restoring after use involves the minimum of labour. The splash-plate D is stationary, and the valve V is pressed firmly against its seat by means of the lever A, which causes the eccentric C to turn and raise the valve. The lever A is held in position by a link L, made of fusible alloy. When the link gives way, the water-pressure forces the valve downwards, causing A to fall. At its lowest position the upper surface

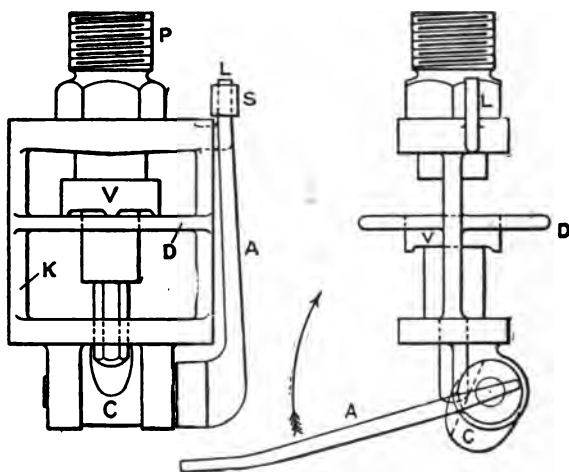


FIG. 57.—WALWORTH'S SPRINKLER.

of the valve V is level with the deflector D, of which it now forms a part. The pipe P, as usual, is connected to the water-supply. The

illustration gives a front view of the sprinkler with the valve closed, and a side view showing the position of the parts when the link has given way.

The "Morris" sprinkler, Fig. 58, is one of the latest forms, and combines simplicity of construction and replacement with a very sensitive action. The valve consists of a hollow cap A, in the interior of which is placed a thin disc of phosphor-bronze, resting on soft metal. The joint is made by pressing this disc against the end of the pipe P, by means of the screw S, which acts through the levers L L. These levers are held in position by the brass strip B, which is made of two pieces, corrugated and soldered together with fusible

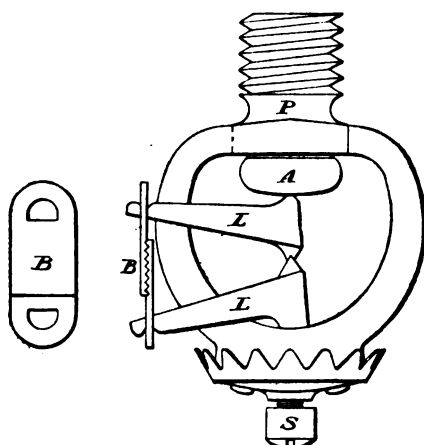


FIG. 58.—THE "MORRIS" SPRINKLER.

alloy, a greater strength being attained than if the surfaces were flat. The levers are independent of each other, save for a bearing surface at the point of contact, made by grooving one lever and making a knife-edge on the other. When the fusible solder melts, the two portions of the link B separate, and the water-pressure pushes the the groove of the upper lever over the knife-edge of the lower. The levers and valve then fall to the ground, and nothing intervenes between the water-supply and the splash-plate. By having the soldered surface at the end of the levers, away from the body of the sprinkler, a more rapid action is secured than occurs when the solder is on the yoke itself, as in the latter case a larger mass of metal must be heated up before the solder melts. After being in action, it is easy

to replace the parts, a number of spare links being kept for this purpose.

Water-sprinklers in general are 3 or 4 inches long, with other dimensions in proportion. It is customary to place them near the ceiling of the room, a short distance apart, so that all come into operation simultaneously and distribute water over the whole room and also on to the ceiling. In some of the earlier forms the water was distributed through a rose, but it was found that the holes frequently became choked with dust, thus greatly impairing the efficiency of the sprinkler. The full discharge of the supply on the splash-plate overcomes this difficulty completely, and is the plan adopted in all modern forms. Another early trouble was the sticking of the valve due to lead being used to make the contact with the seating at the end of the brass supply pipe, as after a time the lead and brass adhered so firmly that the water pressure was insufficient to cause separation, with the result that the sprinkler failed to act. This defect was remedied by the use of Babbitt metal instead of lead; and the more recent plan of making both bearing surfaces of bronze, as in the Morris sprinkler, is better still.

An automatic alarm is generally arranged in conjunction with an installation of sprinklers. When the water in the pipes commences to flow, a bell mechanism is set in motion by the turning of a hinged valve placed in the pipes, or by some similar means; so that the existence of the fire is immediately notified.

The alloy generally used for sprinklers is composed of bismuth, 4 parts (by weight); lead, 2 parts; tin, 1 part; and cadmium, 1 part.

It melts at 150° F., or 65° C., which is well above the limits of atmospheric temperatures, but considerably below the boiling-point of water, and consequently a sprinkler will come into action before a fire has made much progress. The alloy has poor mechanical properties, and when used in the mass tends gradually to flow under pressure. It is difficult to use as a solder, and considerable skill is necessary to fasten two pieces of brass together securely by its aid. As the fusible solder is the vital part of the sprinkler, the soldering operation must be conducted with great care if a successful result is to be obtained.

Other Uses of Fusible Alloys.—Fusible alloys have been employed in the construction of automatic fire-proof doors and screens, which are held back by brass links soldered together with fusible alloy, which on melting, allows a spring or suitable mechanism to close the door or screen. Fusible alloys are also used for sealing joints in cases where a high temperature cannot be employed with safety; and for

obtaining moulds of plaster or clay models in certain electrotyping processes, for which the expansion on solidification, due to the bismuth present, renders these alloys suitable. In all cases where it is desired to take a metal mould at a low temperature, fusible alloys are used.

Fusible Safety-Plugs.—When, from any cause, the water in a boiler runs too low, there is a danger of the upper part of the furnace becoming red-hot, and yielding to the internal pressure. In order to give warning that the water is too low, a fusible plug is fastened into the crown of the furnace, which melts when the temperature rises to a dangerous point, and causes steam to escape into the furnace. These plugs are made by filling holes made in a hollow piece of brass—threaded so as to screw into the crown of the furnace—with lead or suitable alloy. So long as the upper surface of the plug is covered with water, the lead will not melt; but when the water level is below the crown of the furnace, the lead fuses, and the escaping steam gives warning of the danger. The choking of the water-gauge may lead the attendant to believe that the water-supply in the boiler is sufficient, and a serious accident might happen in the absence of a safety-plug to indicate the danger. A temperature of 327°C. , which is the melting-point of lead, cannot be exceeded without warning being obtained. It may be added that the upper side of the plug must be kept free from scale, which would prevent the heat of the furnace passing freely from the lower side to the water, and thus cause premature melting.

Uses of Substances of High Melting-Points. Furnace Linings.—When metallurgical or other operations are conducted at high temperatures, it is necessary to provide an enclosure which will not melt at the temperature employed. Furnaces are therefore built of substances which possess high melting-points, and which are termed “refractory” materials. Carbon, which has the highest melting-point of any known substance, cannot be generally used on account of its tendency to oxidation; in the forms of graphite and gas carbon, however, it is used in some forms of electric furnace. These varieties of carbon oxidise slowly, and, mixed with silica and other materials, are used in the manufacture of crucibles for containing molten metals at very high temperatures. Two chief varieties of linings are used in steel furnaces, the “acid” lining, consisting mainly of silica, and used in the absence of phosphorus; and the “basic” lining, made from dolomite or magnesian limestone, which combines with any phosphorus present in the metal, and hence is used to remove this constituent. Magnesite (magnesium carbonate) is now largely used instead of dolomite, owing to its greater durability. Fire-bricks for

temperatures lower than that of the steel furnace are made from special clays, and in composition are silicates of alumina. The actual melting-points of these materials are not accurately known: that of silica, as used for the "acid" lining, is probably about 2000°C ., whilst that of dolomite is equally high. Magnesite, when calcined, gives off carbon dioxide, and the resulting magnesia is not completely fluid even in the electric furnace, in which the temperature exceeds 3000°C . The most refractory fireclays melt below 2000°C ., the investigations of Seger showing that the clay in which the alumina and silica are present in the proportions of ($1\text{Al}_2\text{O}_3$, 1SiO_2) has the highest melting point, viz., 1890°C .

The necessity of refractory materials possessing much higher melting-points than silica or fireclay, for use in electric furnaces, has largely been met by electric furnace products. When sand and coke are heated together in an electric furnace, combination occurs, with the production of compounds of the two ingredients, varying with the temperature and proportions of the materials. At about 3300°C . the sand and coke form a crystalline compound known as carborundum, which chemically is silicon carbide, SiC , and is practically infusible even in the electric furnace. At 2500°C ., when an excess of sand is used, a body of composition SiCO is obtained, which has been called "siloxicon," and which may be used in a reducing atmosphere up to 3000°C . without decomposition. On breaking up at this temperature, oxygen is given off, and carborundum formed. Both these materials are now largely used as furnace linings; but being comparatively good conductors of heat it is preferable to use them as coatings on fire-bricks rather than in the mass. By the use of such a coating the life of an ordinary furnace lining is greatly increased, as these compounds are unaffected by most of the substances which unite chemically with ordinary refractory materials, and so destroy the lining. The use of carborundum and siloxicon, therefore, is not restricted to the electric furnace, to which, however, they are well suited, owing to being practically infusible. An excellent lining for electric furnaces is also made from magnesite, which is calcined by passing the material gradually through an electric arc. The product, known as "electrically shrunk" magnesite, forms a solid block from which furnace linings may be made, and, if pure magnesite be used, does not melt at the temperature of the electric furnace or that attained by "thermit" compounds.

Utilisation of Latent Heat of Fusion for Heating Purposes. Railway "Foot-Warmers."—It has previously been pointed out that the latent heat disengaged when a liquid solidifies causes the temperature

to remain at the melting-point for a period of time depending upon the quantity of liquid and the rate at which heat is lost by radiation, etc. Advantage has been taken of this phenomenon in the construction of foot-warmers for use on railways, by filling a flat metal vessel with a substance which solidifies at a temperature conveniently warm to the feet. Sodium acetate, which sets at about 60°C ., has been largely used for this purpose by the London and North Western and other railways. The solid is melted in the foot-warmers by steam, and after placing in the compartment the temperature falls gradually until the freezing point of the solid is reached, at which, owing to the large amount of substance used, it remains stationary for several hours. The quantity of heat disengaged in the cooling is much greater than if hot water were used, as in the latter case no latent heat is set free. A drawback to the use of these foot-warmers is the tendency of the salt to become surfused, when, owing to solidification not taking place, the foot-warmer cools sooner than one containing hot water. The tendency to surfusion becomes more marked after repeated meltings, and to ensure solidification an iron ball is sometimes placed in the liquid, which, by rolling about generally causes setting to occur. Shaking the foot-warmer, as many travellers are aware, often causes the temperature to rise, as any form of agitation tends to bring about solidification. The success of these appliances has been greatly discounted by the uncertainty of the setting, and consequent loss of efficiency.

Utilisation of Latent Heat of Fusion for Cooling Purposes.

Freezing Mixtures.—When a solid liquefies, heat is absorbed; and if the process of liquefaction be conducted without external heat being applied to the solid, the heat necessary for the change of state is extracted from the solid itself, and a fall of temperature results. Thus a solid may be caused to liquefy by the addition of another substance, in which case the latent heat of fusion will be extracted from the mixture; and if a lowering of temperature occur, the ingredients form what is known as a “freezing mixture.”

A simple example is furnished by the solution of sal ammoniac in cold water, by means of which a temperature of -10°C . may be attained. The molecules of the solid on dissolving, possess a greater amount of kinetic energy, obtained by extracting heat from the solution—hence the fall of temperature. There is, however, a secondary influence which must be taken into account, namely, the possibility of chemical action taking place between the two substances and the consequent evolution of heat. This is exemplified when caustic soda or potash or anhydrous sodium carbonate are dissolved

in water, as a rise of temperature is then noticed. Generally speaking, therefore, the heat disturbance occasioned when a solid dissolves is the sum of two factors; one, the latent heat absorbed owing to change of state, which tends to lower the temperature; and the other the heat evolved owing to chemical action, which tends to raise the temperature. In freezing mixtures the latent heat absorbed exceeds the heat due to chemical action, and the temperature falls; whilst the converse holds true in other cases, and "heating mixtures" result. In a few instances the two effects are practically balanced, and the temperature therefore does not alter. The heat change may be expressed as follows.

Solution of a solid causes :

$$\begin{array}{cc} \text{A} & \text{B} \\ \left(\begin{array}{c} \text{Heat of chemical} \\ \text{action (+)} \end{array} \right) & \text{and} \left(\begin{array}{c} \text{Absorption of latent} \\ \text{heat (-)} \end{array} \right) \end{array}$$

If A be greater than B the temperature will rise; if B exceed A the temperature will fall.

These considerations explain why only a comparatively few solids are capable of forming freezing mixtures. A table of freezing mixtures is appended, showing in each case the lowering of temperature observed; in the cases in which ice is used, the ingredients are all supposed to be at 0°C . before mixing; in all other instances the starting temperature is taken as 10°C .

TABLE OF FREEZING MIXTURES.

Composition, by Weight	Reduction of Temperature	
	Degrees C.	Degrees F.
Ammonium nitrate 1 } Water 1 }	25.5	46
Sodium nitrate 3 } Dilute nitric acid 2 }	29.4	53
Sal-ammoniac 5 } Saltpetre 5 } Water 16 }	22.2	40
Sodium phosphate 9 } Dilute nitric acid 4 }	34.4	62

TABLE OF FREEZING MIXTURES—*continued.*

Composition by Weight	Reduction of Temperature	
	Degrees C.	Degrees F.
Sodium sulphate . . . 8 } Hydrochloric acid . . . 9 }	27·8	50
Snow or pounded ice . . . 2 } Common salt . . . 1 }	22	39·6
Snow or pounded ice . . . 12 } Common salt . . . 5 } Ammonium nitrate . . . 5 }	31·7	57
Snow . . . 2 } Calcium chloride (crystals) . . . 3 }	45·5	82
Snow . . . 3 } Dilute sulphuric acid . . . 2 }	30·6	55
Snow or pounded ice . . . 5 } Common salt . . . 2 } Sal-ammoniac . . . 1 }	24·4	44

Of all the above mixtures, ice and salt is the cheapest, and although this mixture does not yield the lowest temperature, the quantity of heat absorbed is greater than in the case of equal weights of other mixtures not containing ice. This arises from the superior latent heat of fusion of ice, and it should be clearly understood that the actual temperature obtained is no criterion of the *quantity* of heat absorbed. Guthrie's investigations have shown that a definite limit of low temperature is reached in freezing mixtures, which corresponds to the melting-point of a compound formed in the solution. Ice and salt, for example, when mixed, yield a solution of salt in water, in which a definite compound of the two exists. This compound freezes at -22°C. , and if actual freezing took place, the act would be accompanied by the disengagement of latent heat, which would tend to raise the temperature. In practice, therefore, the temperature cannot fall lower than -22°C. , which represents the lowest limit obtainable with a mixture of ice and salt. The compound formed when ice and calcium chloride crystals mutually liquefy freezes at $-45\cdot5^{\circ}\text{C.}$, which therefore represents the limit for this mixture; and similarly other mixtures have a limit represented by the freezing-point of a compound produced in the solution. Hence the actual temperature obtained is not a measure of the quantity of heat absorbed; and ice and salt,

P

for example, occasion a much greater absorption of heat than phosphate of soda and nitric acid, although the latter mixture yields the lower temperature.

Freezing mixtures are largely employed in the making of iced confections, and in minor cooling operations, ice and salt being used for these purposes on the grounds of cheapness and efficiency. When a specially low temperature is desired, a mixture of ice and crystallised calcium chloride is used. Before the introduction of economic refrigerating machines attempts were made to produce artificial ice on the large scale by the use of freezing mixtures. The general procedure was to dissolve a suitable salt in water—nitrate of ammonium for example—and to pump the cold solution through a series of pipes surrounded by the water to be frozen. The pipes were continued into a second vessel, containing water intended to dissolve the ammonium nitrate, which was thus cooled before use. Finally, the solution was conducted into an evaporating tank, and the salt recovered and used over again. Such a process is continuous, and capable of producing a good supply of ice ; but as the cost of production is greater than when a modern refrigerating machine is used, the method is no longer employed.

CHAPTER XI.

VAPOURS.

Molecular Changes in Liquids due to Heat.—As a general rule, a liquid on heating becomes more mobile, that is, flows more freely. Hence hot liquids pass more readily through the pores of filter-paper, or through a fine orifice, than when cold. This increase of mobility is in all probability due to the increased freedom of motion of the individual molecules, which show a diminished tendency to adhere when the temperature is raised.

In certain cases a rise of temperature induces molecular rearrangement, and thereby causes considerable alterations in the properties of the liquid. A notable instance of such changes is furnished by sulphur, which at 115°C . forms a clear, amber-coloured liquid, which flows readily. On raising the temperature the colour darkens, and the liquid becomes less mobile, until at 230°C . the mass is almost black, and so viscous that it cannot be poured out of a vessel. A further increase of temperature largely restores the mobility, and at the boiling-point— 444.5°C .—the liquid flows with a fair amount of freedom, but still remains black. If cooled, the same changes are observed in the converse order; the progressive alteration in physical properties being in each case due to molecular rearrangement. The great difference in properties of metals and alloys cast at different temperatures may be in part due to the suppression of molecular changes by sudden cooling in the mould, which changes would take place on slower cooling. The solidifying of albumen (white of egg) on heating is a further example of molecular change induced by heat which in this case is permanent in character.

Change of State from Liquid to Vapour.—At all temperatures an unconfined liquid passes into vapour at its surface. Thus a vessel of water, if exposed in dry weather, evaporates completely if left for a sufficient length of time. Other liquids, such as petrol, ether, and alcohol evaporate very rapidly when exposed, and hence are called “volatile” liquids. Even in the case of mercury, the process of passing into vapour at ordinary temperatures, although extremely

slow, may be detected. As the temperature is raised, the rate of evaporation increases, and an increase is also observed when the pressure on the surface of the liquid is diminished.

If the liquid be confined, as in a stoppered bottle, a certain quantity will become vapour and enter the space above the liquid. The molecules of vapour present in the space will exert a pressure on the surface of the remaining liquid in the same way that the molecules of a gas exert pressure; and when the pressure due to the vapour attains a certain value, which for a given liquid at a given temperature is constant, evaporation ceases, or is balanced by an equal amount of condensation. In a closed space, therefore, only a limited amount of vapour can be held at a given temperature, and when this limit has been reached the space is said to be "saturated," and the vapour present in the space is called a "saturated" vapour. If a less quantity than the maximum be present, the space is referred to as "unsaturated," and the vapour itself is also termed an "unsaturated" vapour. As examples, the space above a liquid in a partly-filled bottle is saturated with the vapour of the liquid in the bottle; whilst the atmosphere is usually unsaturated with respect to water vapour, being capable of holding further quantities, as witnessed by the evaporation of an exposed surface of water. As will be seen later, the properties of saturated and unsaturated vapours differ considerably, and it is therefore necessary, in describing the properties of vapours, to take the condition with respect to saturation or otherwise into account.

Pressure of Saturated Vapours.—The pressure exerted by a vapour in contact with its liquid—which is, therefore, a saturated vapour—increases as the temperature rises. The increase in pressure, however, is not uniform; being comparatively small at low temperatures, and large at higher temperatures. When a point is reached at which the pressure of the vapour is equal to that exerted on the surface of the liquid by its surroundings, the liquid gives rise to vapour not only on its surface, but throughout its mass, and is then said to boil. Thus if water in an open vessel be heated when the atmospheric pressure is 760 mm., or 14·7 lb. per square inch, it will boil when the pressure exerted by the escaping vapour is also 760 mm., or 14·7 lb. per square inch. The temperature at which this occurs is 100° C., which is called the boiling-point of water under normal atmospheric pressure. In general, therefore, the boiling point of a liquid may be defined as *the temperature at which the pressure of its saturated vapour is equal to the surrounding pressure*; and consequently any reduction of the latter will

lower the boiling-point, whilst an increase will cause a rise in boiling-point.

A knowledge of the extent of the pressure exerted by saturated vapours at different temperatures is of great importance, particularly in the case of water. Numerical values below 1 atmosphere may be obtained by the apparatus illustrated in Fig. 59, which represents Dalton's method as modified by the author. The barometer tube B, graduated in millimetres, contains a small quantity of the liquid floating on the surface of the mercury, and is surrounded by a water-bath which may be heated by passing steam through the metal pipe P. The mercury in the cistern is brought to the level of the zero mark on the barometer tube by means of the siphon S, the short limb of which terminates at the mercury surface in the cistern, whilst the long limb passes beneath the mercury in the bottle C. On blowing into the bottle by the tube T, the siphon is filled, and on releasing the pressure mercury will siphon over from the cistern into the bottle until the end of the small limb is just above the mercury in the cistern. The siphon is adjusted until the mercury level in the cistern, at the commencement of the experiment, is brought opposite the zero mark on the tube by the action of the siphon. As the temperature rises, mercury leaves the barometer tube and enters the cistern, thereby raising the mercury level above the zero mark; but on working the siphon the surplus mercury passes over into the bottle, and the level again falls automatically to zero. This arrangement enables the height of the mercury in the tube to be read off directly, without requiring a correction for alteration of level in the cistern.

The presence of vapour in the otherwise vacuum space at the top of the barometer tube causes the column of mercury to be depressed, and the amount of depression is a measure of the pressure exerted by the vapour. If no liquid were present, the mercury column would stand at the same height as the barometer; hence the vapour pressure at any given temperature is expressed by the difference between the height of the barometer and the height of the column of mercury

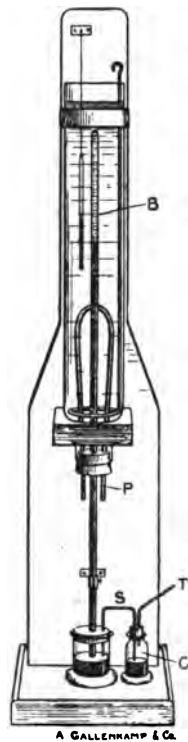


FIG. 59.
APPARATUS FOR DETERMINING THE
VAPOUR PRESSURE OF
WATER BELOW 100° C.

in the tube containing the liquid. In performing the experiment, therefore, the temperature of the bath is raised, and the height of the column of mercury in the tube noted at intervals, care being taken to allow the bath to attain a steady temperature, and to adjust the mercury level in the cistern, before the readings are taken. Each reading, on being deducted from the height of the barometer, gives

the vapour pressure corresponding to the temperature at which the reading is taken. When the temperature rises to the boiling-point of the liquid, the mercury in the barometer tube will be level with the surface of the mercury in the cistern, as, by definition, the pressure of the vapour is then equal to the surrounding pressure, which in this case is 1 atmosphere. In order to obtain this result and adjoining readings it would be necessary to prolong the bath into the cistern; or other methods might be adopted. If very accurate results are required, the height of the column of mercury in the tube should be read off by cathetometer, and corrections applied for the expansion of the mercury. The barometer should also be corrected for temperature, so that the vapour pressures may be obtained in terms of a column of mercury at 0°C .

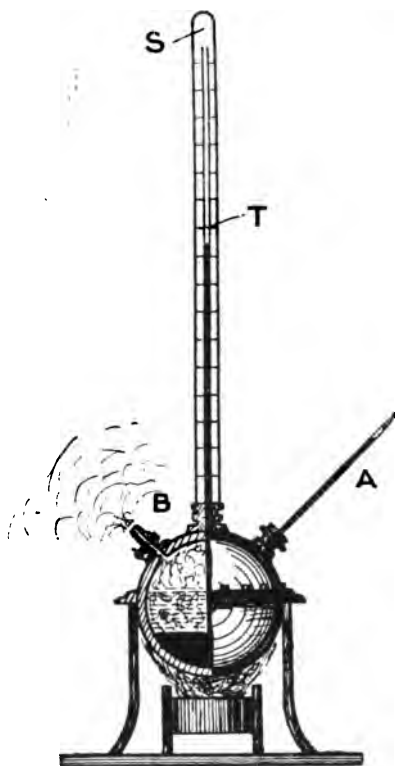


FIG. 60.—MARCET'S BOILER.

When the temperature is such that the vapour pressure exceeds 1 atmosphere, the values may be determined by means of the apparatus shown in Fig. 60, which represents Marcet's boiler. This is a strong steel vessel, in the lower portion of which a quantity of mercury is placed, on the surface of which floats the liquid under test. Through the top of the vessel a stout glass tube T, open at both ends, is passed beneath the mercury surface, and outside the boiler this tube is

fastened to a scale S. A stuffing-gland is provided at the place where the tube enters the boiler, in order to prevent leakage of the vapour, and a thermometer A, is also fixed in the top of the boiler by similar means. The boiler is also furnished with a tap B, which serves to regulate the pressure, and which may be screwed out so as to permit of the introduction of the liquid. In performing the experiment, the liquid is made to boil by means of a Bunsen burner, the tap being kept open. After boiling for one or two minutes, so as to ensure that all air has been expelled by the vapour, the tap is closed, and on continuing the heating the pressure inside the boiler rises, forcing the mercury up the tube. When the column of mercury appears in view outside the boiler, the flame is adjusted until the height of the column is stationary, when the readings on the scale and thermometer are taken. The temperature is then allowed to rise, the flame again adjusted until the column is stationary, and a second pair of readings taken. All heights must be measured from the level of the mercury in the boiler, which represents the zero of the scale. The vapour pressure at any temperature is then found by adding the height of the barometer to that of the mercury column, as the commencing pressure before closing the tap is equal to 1 atmosphere, and at this stage the mercury in the boiler and tube stands at the same level. Corrections are again necessary for the temperature of the mercury, and also for the altering level in the boiler as the mercury rises up the tube. It is not easy to make these corrections accurately, but as the increase of pressure with temperature is relatively large, the corrections do not affect the results to any marked extent, and may be ignored except when very accurate results are required.

In either of the preceding experiments the values obtained are independent of the amount of liquid present, so long as some remains in the liquid state throughout. The pressure is determined by the number of molecules of vapour present in unit space, which is constant for a given temperature. So long as sufficient liquid is present to yield this number, therefore, the same result will be obtained, any liquid beyond this amount remaining as surplus. As distinct from this, however, the weight of the liquid will tend to lower the mercury column in the barometer tube, and to raise it in the Marcet boiler. This may be allowed for when the specific gravity of the liquid is known; thus in a barometer tube a column of water 13.6 mm. long would depress the mercury by 1 mm., whilst a column of alcohol (sp. gr. = 0.79) of length 17.2 mm. would also cause a depression of 1 mm. The actual vapour pressure, however, is quite independent of the quantity of residual liquid.

Saturation Pressure of Water Vapour.—As it will frequently be found necessary in following chapters to perform calculations involving a knowledge of the saturation pressure of water vapour, a table is appended giving the values obtained by Regnault between -10°C. and $+120^{\circ}\text{C.}$ Figures for temperatures above 120°C. will be found in the special steam tables in Chapter XIII.

PRESSURE OF AQUEOUS VAPOUR IN MM. OF MERCURY.

$^{\circ}\text{C.}$	mm.	$^{\circ}\text{C.}$	mm.	$^{\circ}\text{C.}$	mm.
-10	2.08	16	13.54	90	525.39
-9	2.26	17	14.42	95	633.69
-8	2.46	18	15.36	99	733.21
-7	2.67	19	16.35	99.1	735.85
-6	2.89	20	17.39	99.2	738.50
-5	3.13	21	18.50	99.3	741.16
-4	3.39	22	19.66	99.4	743.83
-3	3.66	23	20.89	99.5	746.50
-2	3.96	24	22.18	99.6	749.18
-1	4.27	25	23.55	99.7	751.87
0	4.60	26	24.99	99.8	754.57
1	4.94	27	26.51	99.9	757.28
2	5.30	28	28.10	100	760.00
3	5.69	29	29.78	100.1	762.73
4	6.10	30	31.55	100.2	765.46
5	6.53	35	41.83	100.3	768.20
6	7.00	40	54.91	100.4	771.95
7	7.49	45	71.39	100.5	773.71
8	8.02	50	91.98	100.6	776.48
9	8.57	55	117.48	100.7	779.26
10	9.17	60	148.79	100.8	782.04
11	9.79	65	186.94	100.9	784.83
12	10.46	70	233.08	101	787.59
13	11.16	75	288.50	105	906.41
14	11.91	80	354.62	110	1075.37
15	12.70	85	433.00	120	1489.6

A curve, connecting temperature with the corresponding vapour pressure, is shown in Fig. 61, from which it may be noticed that up

to 40° C. the pressure shows only a small increase with the temperature, but afterwards rises rapidly, as indicated by the increasing steepness of the curve. It should be noted that the vapour pressure does not vanish when the water freezes, as ice at 0° C. gives off sufficient vapour to generate a pressure of 4·6 mm. of mercury in a closed space,

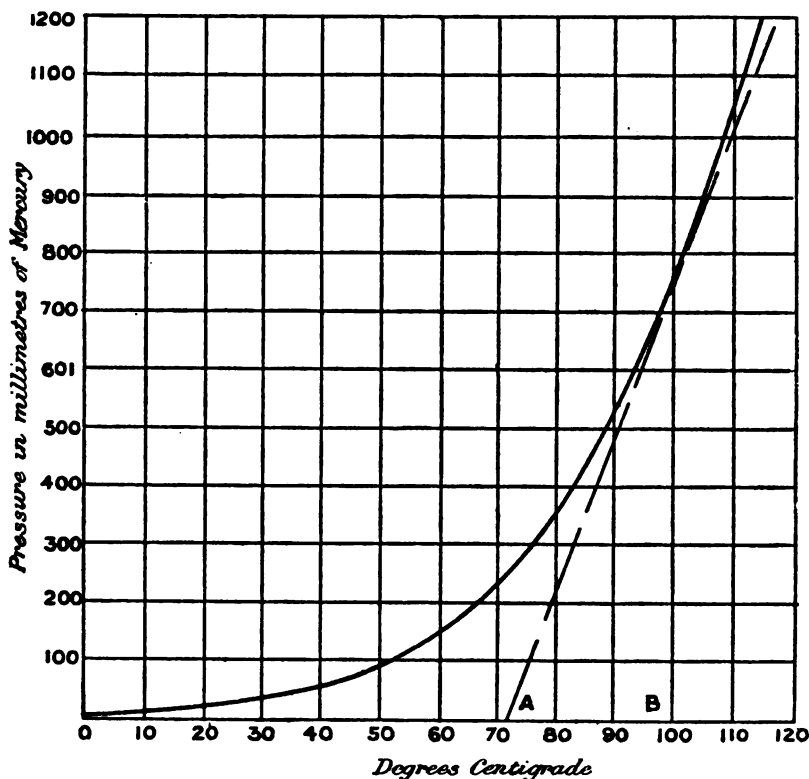


FIG. 61.—CURVE SHOWING VAPOUR PRESSURE OF WATER AT DIFFERENT TEMPERATURES.

and even at -10° C. a pressure of 2 mm. is still observed. No exact equation to this curve is known, but the portion lying beyond 80° C. may be approximately represented by Dulong's formula, which is as follows:—

$$P \text{ (atmospheres)} = \left(\frac{40 + t^{\circ}}{140} \right)^5$$

where t is the temperature in Centigrade degrees.

Pressures calculated from this formula differ by about $1\frac{1}{2}$ per cent. from the observed results at 80° C. and 225° C., whilst the formula is correct at 100° C. Between 100° C. and 80° C. the error rises from 0 to $1\frac{1}{2}$ per cent., and similarly between 100° C. and 225° C. This formula may therefore be used to calculate approximately the temperature in a steam boiler when the pressure is known, or the converse.

Example 1.—If the absolute pressure in a steam boiler be 12 atmospheres (172.4 lb. per square inch), the temperature of the steam will be 190° C., since

$$12 = \left(\frac{40 + t}{140} \right)^5; \text{ and taking logarithms,}$$

$$\log 12 + 5 \log 140 = 5 \log (40 + t), \text{ from which}$$

$$\log (40 + t) = 2.3619$$

and

$$40 + t = 230$$

\therefore

$$t = 190^{\circ} \text{ C.}$$

It must be remembered that absolute pressure = (gauge pressure + 1 atmosphere).

Example 2.—A temperature of 200° C. in a steam boiler will correspond to an absolute pressure of 14.8 atmospheres, or approximately 220 lb. per square inch. The pressure gauge should therefore read 13.8 atmospheres, or approximately 205 lb. per square inch.

As indicated in the two examples, the readings of a thermometer placed in a steam boiler serve as a check on the readings of the gauge, when the vapour pressure of water at different temperatures is known.

The boiling-point of water at any given pressure may be obtained directly from the table of vapour pressures. Thus if the pressure on the surface of water were 433 mm., the water would boil at 85° C., as the vapour pressure of water at 85° C. is 433 mm., and boiling-point is defined as the temperature at which the vapour pressure equals the surrounding pressure. In order to boil water at 0° C., it would therefore be necessary to reduce the pressure on the surface of the water to 4.6 mm., which can be done by special means to be described later. The rate at which the pressure changes at any given temperature may be determined by drawing a tangent to the curve at the point which corresponds to the given temperature. Such a tangent is drawn in Fig. 61, to show the rate of change at 100° C., and on dividing the millimetres represented by the ordinate through

100° by the degrees represented by the distance *AB*, bounded by the ordinate through 100° C. and the point of intersection of the tangent with the horizontal axis, the change is found to be at the rate of 26.8 mm. per degree. This figure has previously been used in Chapter VII. in connection with the correction of the boiling-point of water for small changes of pressure on either side of the normal— 760 mm. A different value will be obtained at other temperatures, as the slope of the curve varies considerably.

The increase of steam pressure with rise of temperature is much greater than that observed with a gas. In order to double the pressure of a gas, initially at 100° C. and one atmosphere pressure, it will be necessary to raise the temperature to 473° C., whereas in the case of saturated steam at 100° C. the pressure becomes 2 atmospheres at 120° C. The reason for this great difference is that in the former case the number of molecules is fixed, whilst in the latter instance a continuously increasing number of molecules enter the space as the temperature rises, and the pressure increases rapidly in consequence. On cooling a saturated vapour, the surplus molecules assume the liquid state, only sufficient remaining in the space as vapour to furnish the pressure corresponding to the existing temperature.

As might be expected, liquids possessing a higher boiling-point than water, such as mercury, glycerine, and strong sulphuric acid, exert a less vapour pressure than water at a given temperature; whilst liquids of lower boiling-point, such as alcohol, ether, and petrol, give higher values than water. The vapour pressure of mercury at ordinary atmospheric temperatures is extremely small—hence its suitability for barometers and for air-pumps. The limit of vacuum obtainable with a pump in which a liquid is used is obviously the vapour pressure of the liquid at the working temperature; thus a pump in which water is present cannot possess, at 15° C., a less internal pressure than 12.7 mm., or about $\frac{1}{4}$ lb. per square inch. It is customary for engineers to speak of the difference between 1 atmosphere and the internal pressure as the “vacuum,” and adopting this mode of expression the best vacuum obtainable in the presence of water at 15° C. is 747.3 mm., or 29.4 inches, when the barometer is at the normal height. The use of a heavy oil in an air-pump enables a very good vacuum to be obtained, owing to the low vapour pressure of the oil; and by the aid of the Fleuss pump, in which the moving parts are oil sealed, the internal pressure of a vessel may be lowered below 1 mm. The highest degree of exhaustion, however, is obtained by means of the mercury pump, which is used in the final stages of the removal of air from incandescent

electric lamps and vacuum tubes. The vapour pressure of mercury at ordinary temperatures is only a minute fraction of 1 mm., and this small pressure exists in the space above the mercury in a barometer, tending to depress the column. The depression caused, however, is so small as to be negligible.

Pressure of Mixed Gases and Vapours. Dalton's Laws.—Many cases arise in which gases and vapours are mixed, e.g. a bottle half-filled with a liquid contains in its upper part a mixture of air and the vapour of the liquid. With a view to discovering whether the pressure due to the vapour is modified in any way by the presence of the gas, Dalton carried out a series of experiments and arrived at the following conclusions, which are known as Dalton's laws :—

1. In any mixture of gases and vapours, each constituent exerts its own pressure independently, and the extent of this pressure is the same that the vapour would exert if present in an otherwise vacuous space. This law does not apply to mixtures in which the constituents act chemically upon each other.

2. The number of molecules of a given vapour which can be contained in a given space is the same whether the space contains the vapour alone, or other gases or vapours in addition.

Several important conclusions may be drawn from these laws. It is evident, for example, that the total pressure exerted by the mixture is the sum of the several individual pressures. If, therefore, one constituent be removed, the pressure will fall by the amount exerted by this constituent, and, assuming Boyle's law to hold for the mixture, the volume will be diminished in a like ratio. This conclusion is of service in correcting the volume of a gas for the presence of water vapour.

Example.—A quantity of gas, collected over water at 15° C., occupies a volume of 250 c.c. Find the volume the gas would occupy if dry, the barometric pressure in each case being 760·7 mm.

The total pressure due to the wet gas (760·7 mm.) is made up of two factors (*a*) the pressure due to the gas molecules, and (*b*) the pressure due to the water vapour molecules. At 15° C. water vapour exerts a saturation pressure of 12·7 mm., hence the pressure due to the gas is (760·7 - 12·7) = 748 mm. If the water vapour could be extracted, the pressure of the gas would fall to 748 mm., provided the volume remained at 250 c.c. If the dried gas were then compressed to 760·7 mm., its volume, by Boyle's law, would become

$$250 \times \frac{748}{760 \cdot 7} = 245 \cdot 8 \text{ c.c.}$$

Another conclusion to be drawn from Dalton's laws is that if a vapour were liberated in a space—whether empty or otherwise—the pressure would increase by the amount due to the vapour. Hence, if a vessel containing ether, for example, be broken in an air-tight space, the pressure in the space would be augmented by an amount equal to the pressure of ether vapour at the existing temperature, provided some of the liquid remained.

Pressure Exerted by Volatile Liquids when Stored.—The safe storage of volatile liquids (i.e. liquids of high vapour pressure) is a matter of considerable importance, particularly when the vapour is inflammable or dangerous, as in the cases of petrol, ether, alcohol and chloroform. Not only must the storage vessel be strong enough to withstand the enhanced internal pressure occasioned by rise of temperature, but an additional margin must be allowed for rough usage during transport. Neglect of these precautions has led to numerous accidents, many of which might have been avoided if the factors which give rise to the increase of pressure on heating had been allowed for in the construction of proper storage vessels.

When a barrel or other receptacle is charged with a liquid, a space must be left at the end, to allow for the expansion of the liquid, before closing. This space, at the moment the bung is inserted, contains a mixture of air and the vapour of the liquid, and the pressure due to this mixture is equal to that of the atmosphere. When the temperature rises, the internal pressure rises owing to three causes, namely (a) the increased vapour pressure of the liquid, (b) the enhanced expansive force of the enclosed air, and (c) the compression of this air due to the expansion of the liquid. The compression of the vapour in the space merely causes a portion to condense, without altering the pressure due to the vapour. The total rise in pressure is therefore determined by these three factors, and with a volatile liquid stored with a small expansion space, may be a considerable amount.

Example.—A cylindrical keg is filled at 20°C. with a liquid which under normal atmospheric pressure boils at 45°C. , and at 20°C. exerts a pressure of 380 mm. To find the internal pressure if the keg be 105 cm. long, the expansion space 5 cm. long, the pressure of the atmosphere at the moment of closing 760 mm., and the coefficient of expansion of the liquid 0.001, when the temperature rises to 45°C.

a. The vapour pressure of the liquid at 45°C. (its boiling point), will be 760 mm., and as the pressure is 380 mm. at 20°C. (the temperature of filling) the increase under this head will be $(760 - 380) = 380\text{ mm.}$

b. The expansive force of the air will be

$$380 \times \frac{273 + 45}{273 + 20} = 412.5 \text{ mm. at } 45^\circ \text{ C.}$$

an increase of 32.5 mm., as from Dalton's law the pressure due to the air in the space at starting is equal to the total pressure less that due to the vapour, or $(760 - 380) = 380$ mm. This pressure, according to the gaseous laws, rises in the direct ratio of the absolute temperatures. As the pressures of the air and vapour are independent each may be considered separately.

c. As the coefficient of expansion of the liquid is 0.001, a column 100 cm. long, when heated through 25° C. , will elongate by $(100 \times 25 \times 0.001) = 2.5$ cm. The space, originally 5 cm. long, will therefore be halved, and the pressure of the enclosed air doubled. The pressure of the vapour will be unaffected by alterations in the space. Hence the pressure of the enclosed air, at 45° C. , will be $(412.5 \times 2) = 825$ mm.

Consequently, the total internal pressure will be 760 mm., due to the vapour, plus 825 mm. due to the enclosed air, or a total of 1585 mm., or 2.08 atmospheres.

It is evident, from the above considerations, that if the space in the storage vessel be freed from air, the internal pressure will be entirely due to the vapour of the liquid. Should the temperature rise above the boiling-point of the liquid, the internal pressure may increase to several atmospheres. Calculations of the pressure, as shown in the foregoing example, involve a knowledge of several constants, and it is better to subject the liquid to an actual test, under the same conditions as those existing in the storage vessel, in order to determine whether a sufficient margin of safety has been allowed. This may be accomplished by means of the apparatus shown in Fig. 62, devised by the author for this purpose. A glass tube, of narrow bore, divided into millimetres, is sealed into a glass vessel of about 250 c.c. capacity, so that the lower end of the tube is just clear of the bottom of the flask. A neck, fitted with a tight stopper which may be fastened down, is inserted at the side of the flask. In performing a test, 100 c.c. of mercury are poured into the flask through the neck, by means of a funnel with a fine stem, after which the liquid under test is added, and the stopper securely inserted. The space left in the flask should bear the same ratio to the volume of the liquid under test as will obtain in the barrel; thus if 150 c.c. be the volume left after pouring in the mercury, the minimum space allowed, calculated from an assumed coefficient of expansion of 0.001 and a possible

rise of temperature of 50°C. , must be 7.5 c.c. to permit of the expansion of the liquid only. If twice this volume be allowed as space—equivalent to $\frac{1}{10}$ part of the length of a cylindrical keg—then the quantity of liquid poured in will be 135 c.c. Before closing the

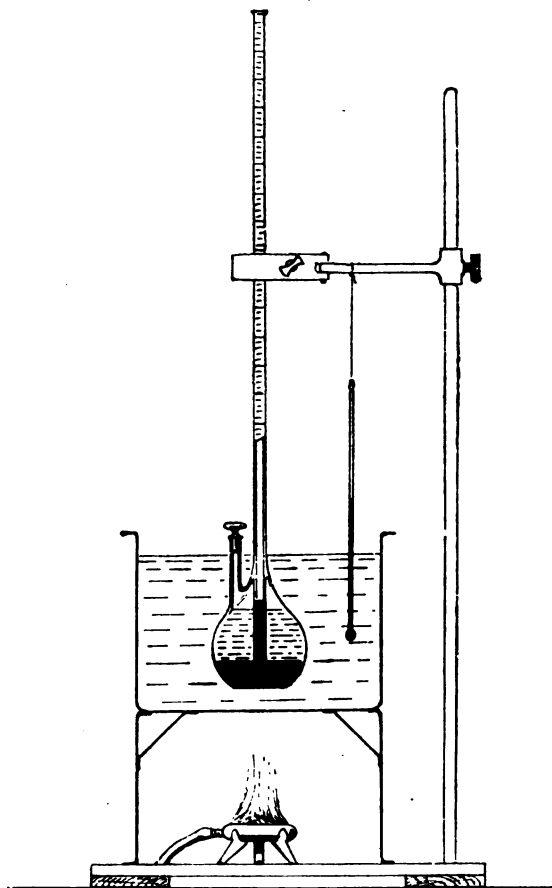


FIG. 62 — APPARATUS FOR TESTING THE STORAGE PRESSURE OF VOLATILE LIQUIDS.

neck, the vessel is placed in a water-bath, the temperature of which is kept at that which is likely to exist during the filling of the barrels. Having attained this temperature the stopper is inserted, and the arrangement is then identical with a vessel filled for storage. The temperature of the bath is then slowly raised to the highest point to

which the liquid will be subject in a hot climate—say 60°C . or 140°F .—or to the highest temperature to which it will be liable. As the temperature rises, mercury will be forced up the tube, and the height of the column, measured from the mercury level in the flask, is read, and corrected, if desired, for the weight of the liquid floating on the mercury in the flask. The total internal pressure will be given by adding the height of the barometer to that of the mercury in the tube, and, if necessary, a series of readings may be taken at different temperatures.

It may not be out of place here to utter a caution against using large quantities of inflammable liquids for such a test as the foregoing, as this procedure has been known to cause loss of life owing to the ignition of vapour which has been allowed to escape, or to the bursting of the vessel and subsequent explosion of its contents. The results obtained with the apparatus described are just as accurate as any which might be determined by the use of a larger quantity; and the test may be conducted without danger.

In storing volatile liquids, therefore, a space must be left in the vessel sufficient to permit of the expansion of the liquid, with a liberal margin to prevent any air remaining in the barrel from being compressed to a dangerous point by the expanding liquid. The strength of the vessel should be such as to enable it to resist a total internal pressure several times as great as the combined air and vapour pressure; and great care should be taken that the bungs or stoppers are secured so as to remain fixed and not liable to leakage at the highest pressures to which the vessel will be subjected. For petrol, kegs or drums of mild steel, closed with a screw stopper fitted with a leather washer, form a safe and convenient means of storage, capable of standing a fair amount of rough usage. It should be remembered that the pressure in a small vessel of petrol or other liquid is the same per unit area as in a large drum, and this and other dangerous liquids should therefore never be stored in weak vessels if subject to high atmospheric temperatures. Neglect of this precaution has been the cause of most of the fires and accidents which have occurred with stored petrol.

Vapour Pressure of a Liquid in Communication with a Cold Space. Watt's Separate Condenser.—In all the instances of vapour pressure hitherto considered, the liquid and vapour have been assumed to be at the same temperature as their surroundings, as also any space containing the vapour. If, however, the space into which a liquid evaporates be colder than the liquid, the pressure exerted by the vapour will be the saturation pressure corresponding to the tempera-

ture of the cold space and not to that of the liquid. Thus if the barometer tube in Fig. 59 were prolonged above the bath, and terminated in a bulb surrounded by ice, the depression of the mercury column would only be 4·6 mm., whatever the temperature of the bath. The reason for this is that vapour given off from the liquid in greater quantity than that required to saturate the space at 0° C. will condense in the bulb, and hence the pressure is determined by the coldest part of the vapour. This is the principle of the "separate condenser" introduced by James Watt in the steam-engine. When the steam in the cylinder is made to communicate with the condenser the pressure falls to that which corresponds to the temperature of the condenser, and the same effect is produced as if the steam were cooled in the cylinder itself.

If the cold portion of the space be small in comparison with the heated portion, as in the case of the barometer tube in Fig. 59 being allowed to protrude just above the surface of the bath, only a slight lowering of the vapour pressure due to the higher temperature is observed, as condensation does not occur to a sufficient extent to reduce the pressure by any considerable amount. The pressure of a vapour is determined by the number of vapour molecules in the space, more being present at high temperatures than at low; and unless the cool part of the space is capable of condensing these molecules to such an extent as to maintain the lower number, the lower pressure will not be reached. Thus the pressure-gauge of a steam boiler records the pressure of water vapour at the temperature existing in the boiler, as the reduction of vapour molecules caused by condensation in the gauge is infinitesimal compared with the total number in the boiler itself.

Differences between Gases and Vapours.—If a given space be capable of holding 1 gram of a certain vapour at a given temperature and only a portion—say $\frac{1}{10}$ of a gram—were actually present, the properties of the vapour under these circumstances would differ in degree only from those of a gas. The vapour would for example approximate less closely to a perfect gas than air or hydrogen. On diminishing the space to $\frac{1}{10}$ its former volume, it would now be charged to its maximum capacity with vapour, and the pressure per unit area will be ten times as great as previously. So long as the vapour remains unsaturated—that is, so long as liquefaction does not commence, it would approximately obey the gaseous laws; and the further the vapour is removed from saturation, the more closely will it approximate in properties to a perfect gas. Inasmuch as a hot space is capable of holding more vapour molecules per unit volume

than a cold space, the effect of heating a vapour apart from its liquid is to remove it further from the state of saturation, and consequently to cause the vapour to obey more closely the gaseous laws. Thus at very high temperatures unsaturated water vapour is a true gas; and conversely, at very low temperatures gases such as air or hydrogen behave as vapours. An unsaturated vapour, therefore, may be regarded as a gas under conditions such that liquefaction may easily be brought about, either by an increase in pressure or reduction of temperature. Gases which are fairly easily liquefied, such as sulphur dioxide and ammonia, are in reality unsaturated vapours not differing greatly in properties from water vapour; and even air and hydrogen under usual atmospheric conditions, merely represent unsaturated vapours at a temperature greatly above the liquefying point. Evidently therefore the state of a gas differs only in degree from that of an unsaturated vapour, and the two cannot be regarded as actually distinct.

When, however, a space becomes saturated—that is cannot hold more molecules in the condition of vapour—an entirely different behaviour is shown by the contained vapour. If, for example, a space at a given temperature be saturated when it contains 1 gram of vapour, and this amount of vapour is actually present, a reduction of the volume will not cause an increase of pressure. On reducing the volume by one-half, vapour to the amount of $\frac{1}{2}$ gram would condense to liquid, leaving the number of vapour molecules per unit volume the same as before. On again increasing the volume to its original size the liquid previously formed will evaporate, and the pressure remain constant owing to this reason. Hence a saturated vapour in no sense obeys Boyle's law, as the pressure is independent of the volume; that is, P (at constant temperature) = a constant. A saturated vapour really represents the transition state between a gas and its liquid, and its properties differ from both. An idea of these differences may be obtained by considering a cylinder, fitted with a pressure-gauge, into which carbon dioxide is continuously pumped. On commencing, the pressure will be observed to rise until a point is reached at which liquefaction occurs. At this point the gauge will remain steady, any gas pumped in being converted at once into liquid, and therefore failing to add to the pressure. When the cylinder is absolutely full of liquid, the pressure will again rise, as the incoming gas now tends to compress the liquid. Conversely, on opening the valve of a cylinder containing liquid carbon dioxide, the pressure remains steady so long as any liquid remains; but after all the liquid has evaporated, the pressure of the residual gas will fall off according to Boyle's law. These observations are shown in graphic form in Fig. 71.

It may again be emphasized that the condition of saturation is determined by the presence of a definite number of molecules per cubic centimetre, which at a given temperature cannot be exceeded. Reduction of volume therefore causes the surplus molecules above this number to settle out as liquid ; and an increase of volume causes more liquid to evaporate until the requisite number are present. In the absence of the liquid, an increase in volume will reduce the number of molecules per cubic centimetre, and the pressure will therefore diminish, and the vapour no longer be saturated. Hence the spontaneous maintenance of a constant pressure at a given temperature distinguishes a saturated vapour from a gas or unsaturated vapour.

Vapour Density.—A knowledge of the vapour density of a substance is of great importance in chemistry, as it furnishes a clue to the molecular weight. Vapour densities may be determined by directly weighing a known volume of the vapour under specified conditions of temperature and pressure ; or by measuring the volume of air displaced when a known weight of liquid is vaporised in a tube containing air, as in Victor Meyer's method. It is customary, for chemical purposes, to express the figure as the weight of the vapour compared with that of an equal volume of hydrogen under the same conditions. Thus by stating that the vapour density of alcohol is 23, is meant that alcohol vapour is 23 times as heavy as hydrogen under the same conditions of temperature and pressure. The density of water vapour and steam are frequently referred to liquid water as a standard, as is usual for solids and liquids. Compared with water at 4° C. as unity, water vapour has a density of .00080 when at a pressure of 760 mm., and a temperature of 0° C. Hence at normal temperature and pressure 1 litre of water vapour weighs .80 gram, and is, therefore, lighter than dry air, 1 litre of which weighs 1.293 grams under the same conditions.

"Flash Point" of Inflammable Liquids.—All inflammable liquids give off vapour, the quantity evolved increasing with the temperature. When the quantity of vapour present in air rises to a definite amount, the mixture explodes on applying a light ; but if the amount of vapour mixed with the air be in less proportion, no explosion occurs. The temperature at which the vapour is liberated in sufficient amount to form an explosive mixture with air is termed the "flash-point." The figure for petroleum is determined by means of the standard apparatus designed by Sir F. Abel, and illustrated in Fig. 63. The petroleum under test is placed in the closed vessel A, and its temperature raised by means of the water-bath B. The lid of the vessel

A is furnished with a sliding-piece which carries a small lamp, and on drawing out the slide the lamp is tilted so that the flame enters the interior of A, when, if sufficient inflammable vapour be present in the space, a flash will be observed. In conducting the experiment the water-bath is raised to a steady temperature (which exceeds the flash-point of the oil under test) and the vessel A then placed in

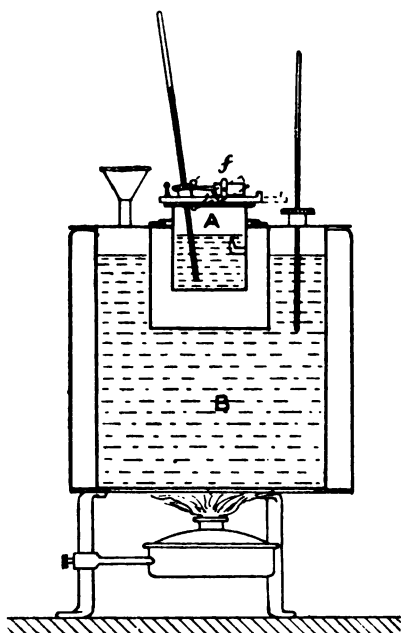


FIG. 63.—ABEL'S FLASH-POINT APPARATUS (Close test).

position. At frequent intervals the slide is withdrawn, until a flash is observed; when the temperature recorded on the thermometer placed in the petroleum is read, and constitutes the flash-point. Abel's apparatus is made to standard size, and to secure uniformity of results must be worked under prescribed conditions as to the starting temperature of the bath, the interval between each withdrawal of the slide, and the size of the flame of the lamp. These instructions are furnished with the apparatus. Burning-oil for use in Britain must not flash at a lower temperature than 73° F.; in other countries a minimum of 100° F. or more is prescribed. It would evidently be dangerous to have a naked flame in the vicinity of oil

stored at a temperature equal to or exceeding the flash-point.

The above method of determining the flash-point is known as the "close" test, as the vessel is shut during the intervals between each application of the flame. The "open" test is frequently adopted for lubricating oils which possess high flash-points. In this test the oil is heated in an open vessel by a small flame, and a lighted taper, or small gas-jet, brought near the surface at frequent intervals until a flash is observed. A thermometer placed in the oil registers the temperature, and is read when the flash is obtained. To secure a sharply-defined result, the rise of temperature near the flash-point should be conducted slowly.

CHAPTER XII.

EBULLITION.

Determination of the Boiling-Point of Liquids.—The boiling-point of a liquid has previously been defined as the temperature at which the pressure of its vapour is equal to the pressure on its surface. The value, therefore, will vary according to the pressure, and the normal boiling-point is taken as the temperature at which the vapour pressure is 760 mm., or one atmosphere. The boiling-point under existing atmospheric conditions may be obtained by boiling the liquid in a flask furnished with a free outlet, and placing a thermometer in the vapour so that the bulb is about 1 inch above the surface of the liquid. The value at 760 mm. may be found by raising or lowering the pressure to 760 mm. by artificial means, or the pressure corresponding to the given boiling-point may be recorded. The thermometer should not be placed in the liquid if this can be avoided, as unless special care be taken this temperature may vary considerably, whereas that of the vapour is constant for a given pressure if the liquid be pure.

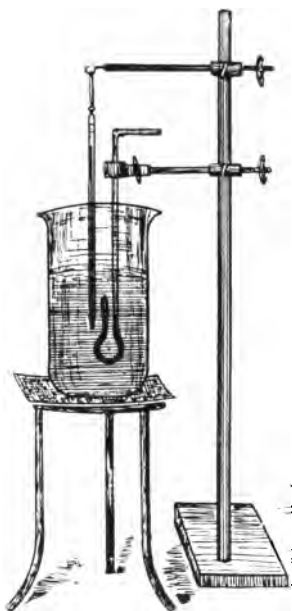


FIG. 64. —DETERMINATION OF THE BOILING-POINT OF A LIQUID.

An alternative method, useful for small quantities of liquids, or for liquids which are dangerous to boil in a flask, is illustrated in Fig. 64.

A glass tube is bent into two parallel branches, the shorter of which is closed, and the longer left open to the atmosphere. A small quantity of the liquid is introduced into the closed limb, so as to occupy the space at the closed end, and the remainder of the tube contains mercury up to some point in the open branch, so that the level is below that in the closed branch. The tube is now immersed in a bath, and the temperature raised until the mercury is level in both limbs. The temperature of the bath is then the boiling-point of the liquid at existing atmospheric pressure, as the pressure of the vapour in the closed limb is then equal to that exerted by the atmosphere down the open limb. To find the normal boiling-point, it is only necessary to take a reading of the temperature of the bath when the vapour pressure of the liquid is 760 mm. Thus if the atmospheric pressure at the time of the experiment be 750 mm., the heating is continued until the mercury in the open limb is 10 mm. above that in the closed limb; when the pressure exerted by the vapour will be $(750 + 10) = 760$ mm. The last stages of the heating should be conducted very slowly to ensure an accurate result.

The following table gives the boiling-points of a number of liquids at normal atmospheric pressure :—

Liquid	Boiling Point in	
	Degrees C.	Degrees F.
<i>Ordinary Liquids—</i>		
Ether	35	95
Carbon disulphide	46·2	115
Chloroform	61·2	142
Alcohol	77·9	172·2
Benzene	80·4	176·7
Water	100	212
Turpentine	159	318
Aniline	184	363
Naphthalene (solid to 82° C.)	220	428
Glycerine	290	554
Olive-oil	315	599
Strong sulphuric acid	325	617
Mercury	357	675
Sulphur (solid to 114·5° C.)	444·6	833

Liquid	Boiling Point in	
	Degrees C.	Degrees F.
<i>Liquefied Gases—</i>		
Sulphur dioxide.	— 10	14
Ammonia	— 34	— 29
Carbon dioxide	— 78	— 108·5
Liquid air,	— 191·5	— 313
Oxygen	— 182·5	— 296
Nitrogen	— 193	— 315·5
Argon	— 186	— 303
Hydrogen	— 252·5	— 422

A definite boiling-point cannot in most cases be assigned to a mixture of liquids, such as go to form petroleum. In such cases, if heat be gradually applied, the thermometer will remain fairly steady for a time, and a portion of more or less definite composition will evaporate; after which the thermometer rises to some higher temperature, and again remains nearly steady. Several successive readings may thus be obtained, corresponding to the boiling-points of the various fractions. The temperature at which the vapour pressure of the mixture is equal to 760 mm. can, however, be obtained by means of the bent tube method used to determine the boiling-points of pure liquids (Fig. 64). Only in rare cases does a mixture possess a constant boiling-point.

Effect of Pressure on the Boiling-Point.—The lowering of boiling-point caused by reduction of pressure may readily be demonstrated by placing a beaker of warm water under the receiver of an air-pump, and exhausting the air. When the pressure is reduced to such an extent as to be equal to the vapour pressure of the warm water, rapid boiling will be observed. The same phenomenon is observed in the experiment due to Franklin, in which water is boiled in a flask until the air is expelled, and the flask then corked up. On cooling the flask by pouring water over it, the steam in the interior condenses, and thus lessens the pressure on the contained hot water, which then boils vigorously. Hence the seeming paradox of the water boiling owing to the cooling of the flask.

The rise of boiling-point under increased pressure may also be simply demonstrated by heating water in a flask furnished with a cork, and a bent outlet-tube which dips under a column of mercury.

through which the steam must escape. As the length of the mercury column is increased, a thermometer in the interior of the flask will show a progressive rise of temperature. Similarly, the water in a steam boiler increases in temperature as the pressure rises.

The reduction of boiling-point under diminished pressure is taken advantage of in the evaporation of liquids at a low temperature, in cases where a temperature equal to the normal boiling-point is undesirable. In the manufacture of sugar the solutions are boiled in air-tight vessels, known as vacuum-pans, the pressure in the interior of which is reduced so that the solution boils at about $70^{\circ}\text{C}.$, exhaust pumps being employed for the purpose. The same process is employed in the preparation of many chemical substances which would undergo decomposition at the normal boiling-point of the mother liquor. The drying of substances at a low temperature can be rapidly accomplished in a similar manner. In many cases it is desirable to raise the boiling-point—for example, in the cooking of food at high altitudes, where the pressure is low and the boiling-point below the normal in consequence. Foods such as eggs and vegetables cannot be properly cooked unless the temperature borders on $100^{\circ}\text{C}.$; hence boilers, fitted with an adjustable valve, are used as cooking vessels, the valve being arranged to blow off at $100^{\circ}\text{C}.$ Such boilers are known as “digesters,” and are also used in the conducting of chemical processes in which the desired reaction only occurs above the normal boiling-point of the solution used.

Determination of Altitudes by Observations of the Boiling-Point of Water.—On ascending into the atmosphere the pressure diminishes, and consequently the boiling-point of water will be lowered. The barometric pressure at a given elevation may be determined by observing accurately the temperature at which water boils, and referring to a table of vapour pressures; for the vapour pressure at the boiling-point observed is equal to the surrounding pressure. Thus if the water boiled at $95^{\circ}\text{C}.$, its vapour pressure— 633.7 mm. of mercury—must also represent the atmospheric pressure. The height may then be deduced from the tables employed for obtaining elevations by the aid of a barometer. When only an approximate result is required, it may be assumed that an elevation of 900 feet causes a fall of $1^{\circ}\text{C}.$ in the boiling-point of water. The apparatus employed consists of a boiler furnished with a long, telescopic tube, in which a delicate thermometer may be placed so as to be surrounded by steam, which escapes at the top of the tube. In order to ensure an accurate reading, the thermometer is constructed so that the lowest mark on the scale represents $85^{\circ}\text{C}.$, and the highest

105° C., the whole stem thus being covered by a range of 20°, and consequently capable of fine sub-division. The apparatus is known as the *hypsometer*, or height-measurer, and is obviously more portable than the mercury barometer, which it was designed to supersede for this purpose. It is, however, much inferior in this respect to the aneroid barometer, and its use is now restricted to checking the readings of the latter type of barometer.

Effect of Dissolved Solids on the Boiling-Point.—The boiling-point of a liquid is invariably raised when a solid is dissolved in it, and consequently the vapour pressure is lowered. The rise in boiling-point is progressive as the amount of dissolved solid present in a given volume of liquid is increased, and reaches a maximum when saturation occurs. The rise in boiling-point, moreover, bears a definite relation to the molecular weight of the dissolved solid. Taking 100 c.c. of water as the standard, the rise occasioned by 1 gram-molecule of any salt is approximately 10° C. Thus the molecular weight of calcium chloride (CaCl_2) is 111, and of sodium nitrate (NaNO_3), 85; and if 111 grams of calcium chloride and 85 grams of sodium nitrate each be dissolved in separate 100 c.c. of water, the boiling-point of the solution in each case will be 110° C. at 760 mm. pressure. With non-electrolytes, such as sugar, the molecular rise is only one-half that occasioned by salts, or 5° C.

In taking the boiling-point of a solution the thermometer bulb must be placed in the liquid, as the temperature of the steam is intermediate between those of the solution and the pure liquid, owing to condensation and evaporation taking place on the thermometer bulb. A piece of platinum wire placed in the solution ensures steady boiling.

Normal and Abnormal Boiling.—When a vessel containing a liquid is heated from below, the layer of liquid nearest the flame becomes hotter than the rest and rises, colder liquid falling to take its place. A circulation is thus set up, and the temperature of the whole mass is raised. After a time large bubbles of vapour are observed to form in the layer nearest the source of heat, which rise towards the surface, but condense before reaching it owing to the lower temperature of the upper portions of the liquid. This condensation is accompanied by a noise known as “singing,” due to the liquid being set into a state of vibration by the collapsing of the bubbles. Finally, the bubbles of vapour are no longer condensed by the overlying liquid, which has now become too hot to effect the condensation; and consequently the bubbles reach the surface and pass into the space above. The liquid is then said to boil, or to be in a state of ebullition.

If a thermometer be placed in a boiling liquid its readings will be practically steady until all the liquid has boiled away. This is owing to the fact that the heat energy of the flame is converted into kinetic energy in order to bring about the change of state from liquid to vapour, and a stationary temperature results as in the case of a melting solid. The temperature of the boiling liquid is not quite the same at all parts, although, owing to the thorough mixing caused by the vapour bubbles, the variation is but slight, the highest temperature being recorded nearest the source of heat. Hence one reason why in standardising a thermometer the temperature of the steam, and not of the water, should be taken.

Under special conditions, however, the boiling of a liquid may take place in a manner very different to the foregoing. Water, for example, normally contains a quantity of dissolved gases, which may be driven off by prolonged boiling. When all the gases have been expelled, the numerous vapour bubbles previously observed cease to be evolved, and the temperature rises considerably above the usual boiling-point. Ultimately a layer of vapour is suddenly formed over the portion of the vessel in contact with the source of heat, and this layer of vapour is frequently of sufficient dimensions to lift the overlying liquid bodily, and sometimes to eject it from the vessel. This violent boiling is known as "bumping," and is particularly noticeable in the case of liquids of an oily character, such as strong sulphuric acid, solutions of caustic soda and potash, olive-oil, linseed-oil, and heavy oils generally. The explanation of this abnormal boiling is that dissolved gases, when present, serve as nuclei round which vapour bubbles readily collect, but in the absence of such nuclei the formation of vapour is less easily accomplished and only takes place at a higher temperature, at which vaporisation occurs simultaneously over the hot part of the vessel. Donny, Dufour, and others have shown that the temperature of water may be raised to 140°C. , and even higher, without boiling, although the pressure is kept normal.

When it is necessary to boil liquids which are specially liable to exhibit the phenomenon of bumping, tranquil boiling can generally be ensured by bubbling air continuously through the liquid; or by using a ring burner, which heats the upper portions of the liquid and obviates the danger of ejection. On the small scale bumping can be prevented by introducing a few pieces of clay tobacco pipe stem, or a piece of platinum wire into the liquid, the air contained in the pores of the former, and the gases occluded by the latter, serving as nuclei round which the vapour can collect. On the commercial scale pieces of silica firebrick serve the same purpose, but in all cases, when the gases

have been expelled, bumping will recur, and fresh deterrent material must be added.

The phenomenon of suspended boiling is analogous to the reluctance to melting occasionally shown by solids, and to the surfusion of liquids. In each case the change of state is retarded unless assisted extraneously.

Spheroidal State.—When a drop of water is allowed to fall on a very hot metallic surface, it does not spread out into a thin layer, but assumes a spheroidal form, and either rolls about or rotates on its axis. The globule does not touch the plate, as may be observed with the naked eye. Moreover, the temperature of the globule is less than the boiling-point of water, which may be proved by placing a small thermoelectric junction in the interior, when a temperature as low as 96°C . may be observed. The spheroid evaporates away tranquilly, no signs of “steaming” being visible, but if the plate be allowed to cool to 150°C ., or thereabouts, the water comes into actual contact with the surface and spreads out, the contact being accompanied by a hissing noise and the evolution of a cloud of steam. Many other liquids behave in a similar manner to water.

When a piece of red-hot iron is plunged into water, a layer of vapour forms round the metal, which does not actually touch the liquid until the temperature has fallen considerably, and a similar layer of vapour exists between a globule of liquid and a hot plate. No satisfactory explanation of these phenomena has yet been given.

It has been suggested that boiler explosions may occasionally be due to the water entering the spheroidal state in the vicinity of the heating surface. If coated with scale internally, it is possible that the plates may become very hot on the inner side, being protected from contact with the water by the scale, which is a bad conductor of heat. The effect of heating is to cause the scale to chip off, and the water, being presented to the hot surface, would assume the spheroidal state. On the plate cooling sufficiently to permit of actual contact with the water, a sudden generation of steam would occur, and the pressure might rise to such an extent as to burst the boiler before the steam had time to escape through the safety-valve.

CHAPTER XIII.

LATENT HEAT OF VAPORISATION. PROPERTIES OF STEAM.

Latent Heat of Vaporisation.—The change of state from liquid to vapour is accompanied by an absorption or disappearance of heat energy, which confers on the molecules of the vapour a greater kinetic energy than that possessed in the liquid state. One volume of water yields nearly 1700 volumes of steam at 100°C. , and it is therefore evident that the molecules of the steam move over much longer paths than those of the liquid, the extra energy necessary to accomplish this being derived from the source of heat. The heat energy thus expended is termed “latent heat of vaporisation,” and is expressed numerically as *the number of heat units required to convert unit weight of a liquid into vapour, without change of temperature.* An equivalent definition is *the number of heat units evolved when unit weight of vapour condenses to liquid, without change of temperature.* The figure may be expressed in terms of calories per gram ; $\text{lb.}^{\circ}\text{C.}$ units per pound, or British thermal units per pound.

The latent heat of steam at atmospheric pressure may be determined by passing dry steam from a small boiler into a known quantity of water contained in a calorimeter. The rise in temperature is noted, and the weight of steam condensed determined by weighing the calorimeter and its contents at the end of the experiment, when the increase in weight will represent the condensed steam. The method of calculating the result is shown in the following example.

Example.—A calorimeter, of water equivalent 19 grams, contains 450 grams of water at 15°C. Steam at 100°C. is passed in, and the temperature rises to 36°C. The increase in weight of the calorimeter and water is 16.4 grams. To find the latent heat of steam at 100°C. :—

Let L = the latent heat = the number of calories given out when 1 gram of steam at 100° condenses to water at 100° .

Total heat units given out by steam	Heat units gained by water and calorimeter
$16 \cdot 4 \times L = \text{calories given out in}$ $\text{condensing to water at } 100^{\circ}$	$(450 + 19) \times (36 - 15) = \text{calories}$
$16 \cdot 4 \times (100 - 36) = \text{calories given}$ $\text{out by resulting water on cool-}$ $\text{ing from } 100^{\circ} \text{ to } 36^{\circ}$	$\text{gained by water and calori-}$ meter

Equating, $16 \cdot 4 L + 16 \cdot 4 (100 - 36) = 469 (36 - 15).$

From which $L = 536 \cdot 5$ calories per gram.

The chief source of error in the experiment is the presence of water particles in the steam, which add to the weight of the latter. By passing the steam through an oil bath, kept at 110°C. , this error can be avoided, and the additional heat liberated may be allowed for in the calculation by multiplying the weight of steam by its specific heat ($\cdot 48$) and the fall in temperature from that of the oil-bath to the temperature of condensation. This quantity would be placed on the left-hand side of the equation in the foregoing example.

The latent heat of vaporisation of other liquids may be found in the same manner, allowing the vapour to condense in a known weight of its own liquid in a calorimeter. The specific heat of the liquid must be known in order to obtain the number of heat units given out after condensation, and also the heat units gained by the cold liquid. The equation would then become :—

(Weight of vapour condensed $\times L$) + (Weight of vapour \times sp. ht. of liquid \times fall in temp.) = (Weight of liquid \times sp. ht. \times rise in temp.) + (Water equiv. \times rise in temp.). From this L may be obtained by calculation. Or the vapour may be allowed to condense in water, if it be certain that no chemical action takes place between the vapour and water. A table of latent heats of evaporation of different liquids, when evaporating under a pressure of 760 mm., is appended (page 238).

It will be observed that water possesses a higher latent heat of vaporisation than any other liquid, and consequently requires more heat to be converted into vapour. Conversely, when steam condenses, the amount of heat disengaged is greater, weight for weight, than in the case of any other vapour. Hence the superior cooling power of evaporating water, and heating power of condensing steam. An idea of the amount of energy involved in the change of state may be obtained by converting the heat units into work units, when it

will be seen that the evaporation of one pound of water at 100°C . absorbs $967 \times 778 = 750,000$ ft.-lb. (approx.).

Liquid	Latent Heat of Vaporisation at 760 mm. Pressure	
	Calories per Gram	B.Th.U. per Pound
<i>Ordinary Liquids—</i>		
Water	537	967
Alcohol (ethyl)	209	376
„ (methyl)	264	475
Ether.	91	164
Carbon disulphide	87	157
Mercury	62	112
Turpentine	74	133
Sulphur (solid to $114^{\circ}\cdot 5$)	363	654
<i>Liquefied Gases—</i>		
Air	55	99
Carbon dioxide	49	88
Ammonia	295	531
Oxygen	56	101
Hydrogen	200	360

Effect of Temperature of Boiling on Latent Heat.—The temperature at which a liquid boils depends upon the pressure, and it is found that the latent heat of vaporisation of liquids is greater when boiling occurs at a low temperature (or pressure) than is the case at a higher temperature (or pressure). Thus the latent heat of vaporisation of water boiling at 0°C . is $606\cdot 5$ calories per gram; at 100°C . 537 calories per gram; and at 150°C ., 502 calories per gram. A falling off in the value of the latent heat is similarly observed with all liquids when the boiling-point is raised by increasing the pressure. This result might be anticipated, as a rise in temperature signifies an increase in the kinetic energy of the molecules, which consequently require less additional energy to enable them to become vapour.

In the case of steam, Regnault found that up to 230°C . the latent heat of vaporisation is closely represented by the equation

$$L = 606\cdot 5 - \cdot 695 t,$$

where t is the temperature at which boiling occurs. If this equation held true at all temperatures, L would become zero at 873°C. ; but the zero value is actually attained at 365°C. , which is the critical temperature of water. Hence above 230°C. the value of L must diminish at a much greater rate than is indicated by the above equation.

Total Heat of Saturated Vapours.—The amount of heat required to convert unit weight of liquid at 0°C. into vapour is termed the “total heat” of the vapour. It evidently comprises the heat required to raise the liquid from 0°C. to the boiling temperature, and the latent heat absorbed in boiling. Thus to raise 1 gram of water from 0°C. to 100°C. requires 100 calories; to evaporate it at 100°C. requires 537 calories; hence the total heat of steam at 100°C. is 637 calories.

The total heat of steam, up to 230°C. , was found by Regnault to be expressed by the formula

$$Q = 606.5 + .305 t,$$

where t is the temperature at which boiling takes place. But since Q is composed of two quantities, viz. latent heat and heat required to raise the liquid from 0° to t° , it follows, if C represent the latter quantity, that

$$L + C = 606.5 + .305 t,$$

or

$$L = 606.5 + .305 t - C.$$

But to raise unit weight of water 1°C. requires 1 heat unit, and hence a rise of t° will require t units; therefore $C = t$. Hence the equation becomes

$$L = 606.5 + .305 t - t,$$

or,

$$L = 606.5 - .695 t$$

which is the formula previously used for the latent heat of steam.

From the above expression the quantity of heat required to convert water at any temperature into steam may easily be calculated. Thus if the feed-water of a boiler be at a temperature of 15°C. , and the temperature of the steam produced be 140°C. , the total heat at the latter temperature will be 648 calories per gram, or $\text{lb.}^{\circ}\text{C.}$ units per pound. But the total heat is measured from 0°C. , and as the water commences at 15°C. the actual amount of heat required will

be $(648 - 15) = 633$ calories per gram, or lb.-°C. units per pound. Or, in general, the heat required to convert 1 lb. of water at a temperature t into steam = (total heat - temperature of water in °C.) lb.-°C. units.

In expressing the total heat of steam in British thermal units per pound, the quantity is frequently reckoned from 0° F. No useful purpose is served by adopting this temperature, at which water would exist as ice, and consequently the latent heat of fusion should be taken into account, as well as the fact that the specific heat of ice is only 0.52. In many tables, however, both these points are ignored,

PROPERTIES OF SATURATED STEAM.

Absolute Pressure in Lb. per Square Inch	Boiling Point in Degrees C.	Total Heat in Calories per Gram or Lb.-°C. Units per Lb.	Total Heat in B.Th.U. per Lb. (from 32° F.)	Weight of 1 Cubic Foot in Lb.	Volume of 1 Lb. in Cubic Feet
0.177	10	610	1098	0.00057	1752
0.333	20	613	1103	0.00109	927
0.612	30	616	1108	0.00184	544
1.06	40	619	1114	0.0031	322.5
1.78	50	622	1119	0.0056	178.5
2.88	60	625	1124	0.0083	120.5
4.50	70	628	1129	0.0124	80.7
6.85	80	631	1135	0.0186	53.8
10.18	90	634	1140	0.0268	37.2
14.7	100	637	1145	0.0380	26.2
20.6	110	639	1150	0.0525	19.1
28.8	120	642	1155	0.0714	14.0
39.2	130	645	1160	0.0955	10.5
52.5	140	648	1165	0.126	7.95
69.1	150	651	1170	0.163	6.14
89.7	160	654	1175	0.208	4.81
114.7	170	656	1180	0.263	3.80
145.5	180	659	1185	0.329	3.20
182.2	190	662	1190	0.406	2.46
226.2	200	664	1195	0.495	2.02
276.1	210	667	1200	0.575	1.74
336.3	220	669	1205	0.695	1.44
404.0	230	672	1210	0.815	1.23

and it is assumed that the water exists as liquid down to 0° F. Such an assumption is misleading, and tables based upon it are incorrect, as they do not give the total heat as previously defined. An abridged table of the properties of saturated steam is given on page 240, in which the total heat is reckoned from 0° C., or 32° F., and in which other useful constants are also given.

Superheated Steam.—If saturated steam be raised in temperature, out of contact with the water from which it is generated, it is said to be superheated. In this condition it is really unsaturated, as the number of molecules per cubic centimetre is less than the maximum at the higher temperature. Superheating may be carried out by passing the steam through pipes heated externally, and in engines using superheated steam this is effected by allowing the steam pipe to pass through the furnace on its way to the cylinder, or through a special superheater. A higher working temperature is thus secured without causing a corresponding increase in the boiler pressure, and any water mixed with the steam is evaporated. The limit of superheating is the temperature at which the materials in contact with the steam are deleteriously affected.

Moisture in Steam from Boilers.—Saturated steam, as generated in a boiler, is seldom free from particles of liquid, which may be entangled mechanically as the steam forms, or arise from condensation due to a subsequent fall in temperature. The moisture present in steam is referred to as “priming water,” and may be determined by one of the three following methods:—

Method I.—Steam from the boiler is passed into a known quantity of water, and the rise in temperature and weight of steam condensed are noted. If the steam were pure, the heat gained by the water and vessel would exactly equal the calculated amount that should be given by the known weight of steam; any deficiency observed is due to moisture, and furnishes a clue to the amount present.

Example.—2 lb. of steam, at a pressure (absolute) of 114·7 lb. per square inch, are passed into 100 lb. of water at 10° C., the water equivalent of the vessel being 2 lb. The temperature rises to 22·3°. To find the percentage of moisture.

From the table on page 240, the temperature corresponding to a pressure of 114·7 lb. per square inch is 170° C., and the total heat at 170°, measured from 0° C., is 656 lb.-°C. units per pound. The latent heat is therefore (656 - 170) = 486 lb.-°C. units per pound. Equating heat lost by steam to heat gained by water and vessel, we have

$$(2 - x) \times 486 + 2 (170 - 22\cdot3) = 102 \times (22\cdot3 - 10),$$

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where x = weight of water in the steam. This gives the value of x to be $\cdot 0263$ lb.; or,

$$\frac{\cdot 0263 \times 100}{2} = 1.315 \text{ per cent.}$$

No accuracy can be secured by this method unless very large quantities are worked with, and a very delicate thermometer used. If, in the above example, the final temperature recorded were 22.4 , or only $\frac{1}{10}$ degree higher, the percentage of water calculated would be $\cdot 247$, or less than $\frac{1}{3}$ of the figure previously obtained. It is evident, therefore, that a slight error of observation may cause a great discrepancy in the result.

Method II. The "Throttling" Calorimeter.—Steam from the boiler is allowed to escape from an orifice $\frac{1}{8}$ of an inch in diameter, the temperature being observed on each side of the orifice. After escaping, the steam expands to atmospheric pressure, and is no longer saturated; any moisture present is therefore evaporated. The greater the amount evaporated, the lower will be the reading on the thermometer placed on the low-pressure side of the disc. The thermometer on the high-pressure side serves to record the temperature of the steam before expanding; and the amount of moisture present may be deduced from the combined readings of the two thermometers. As no heat is supposed to be lost owing to extraneous causes, such as radiation, it may be assumed that the total heat of the mixture of steam and water is the same before and after escaping. The total heat of the escaping steam will be

(Total heat at atmospheric pressure, or at 100° C., + heat given out on steam cooling to 100° C.)

or

$$637 + \cdot 48 (t - 100) \text{ calories per gram}$$

where t is the reading of the low-pressure thermometer, and $\cdot 48$ the specific heat of steam. The total heat of the steam and water before escaping will be $H - xL$, where H = total heat of *dry* steam at the boiler temperature, x = weight of water present in 1 gram, and L = latent heat of steam at boiler temperature; both heat quantities being expressed in calories per gram. Equating,

$$H - xL = 637 + \cdot 48 (t - 100)$$

$$\text{and } x = \frac{H - 637 - \cdot 48 (t - 100)}{L}$$

Example.—To find the percentage of moisture when the temperature before throttling is $180^{\circ}\text{C}.$, and after throttling $126^{\circ}\text{C}.$ From the table the total heat of steam at $180^{\circ}\text{C}.$, is 659, and the latent heat $(659 - 180) = 479$ calories per gram. Inserting in the above expression, $x = .02$, or 2 per cent.

This method is much more reliable than (I.) as a small error of observation in the temperature makes only a little difference in the result. To obtain a fair estimate of the percentage of moisture the steam should be passed for several minutes, and the average temperatures taken over the whole period.

Method III. The "Separating" Calorimeter.—In this method the particles of water are separated mechanically from the steam, and the quantity of moisture obtained by direct measurement. The apparatus used consists of a double cylinder, the inner of which is furnished with a perforated cup, fitted with small baffle-plates at its upper end, and connected at its lower end with a gauge-glass placed outside the apparatus, by means of which the height of the water in the interior may be observed. The outer cylinder is furnished with an inlet at the upper end, which delivers steam into the bottom of the perforated cup, and an outlet at the lower end; a pressure-gauge is also fitted, graduated so as to read pressures and quantities. On admitting steam to the apparatus, any moisture present settles on the sides and baffle-plates of the perforated cup, and trickles down to the bottom of the inner cylinder. The dried steam rises vertically from the cup and passes round the inner cylinder, finally escaping at the outlet. The inner vessel and gauge-glass are calibrated so that a scale, placed behind the glass, reads the weight of water, in pounds, corresponding to given levels, and hence the weight condensed in a given experiment may be read off directly. The pressure-gauge is graduated by allowing steam at a known pressure to flow through for a given time, the escaping steam being condensed and weighed. As the amount of steam escaping through an orifice is proportional to its absolute pressure (provided the opposing pressure does not exceed $\cdot 6$ of the steam pressure, according to Napier's law), one good reading will suffice to graduate the whole gauge. Thus if the absolute pressure ($=$ gauge pressure $+ 14\cdot 7$ lb. per sq. in.) be 95 lb. per sq. in., and 4·5 lb. of steam are condensed in 20 minutes, the mark on the gauge corresponding to $(95 - 14\cdot 7) = 80\cdot 3$ lb. may be marked $\cdot 225$, meaning $\cdot 225$ lb. per minute, or 4·5 lb. in 20 minutes. An absolute pressure of 190 lb. per sq. in., or 175·3 on the gauge, would give a flow of 9 lb. in 20 minutes, and this point on the gauge would be marked $\cdot 45$ lb. per minute; and similarly over the whole scale.

Hence the steam passing in a given time may be read off by multiplying the reading on the gauge by the time in minutes.

Example.—On passing steam through the calorimeter for 25 minutes, .15 lb. of water was collected in the inner vessel, whilst the pressure-gauge indicated that 5.45 lb. of steam had passed through the orifice during the test. The total weight of the wet steam was $(5.45 + .15) = 5.6$ lb., and the percentage of moisture

$$\frac{.15}{5.6} \times 100 = 3.68.$$

In all cases where the sample of steam is taken from a pipe, instead of from the boiler directly, a vertical pipe should be chosen when possible, and the take-off tube inserted so as to terminate in the centre of the pipe. A sample drawn from a spot near the wall, especially in the case of a horizontal pipe, would give too high a result, owing to the greater condensation which takes place on and close to the wall of the pipe.

Dryness Fraction.—The condition of steam with respect to the moisture present is frequently expressed in the form of a “dryness fraction.” This fraction for dry steam would be 1; for steam containing 2 per cent. of moisture .98; and so on.

Use of Steam for Heating Purposes.—Buildings are sometimes heated by means of steam pipes, connected with a suitable boiler and furnished with cocks from which the condensed water may be drawn off. This method is economical if waste steam be utilised for the purpose, but hot-water circulation is generally preferred to the special generation of steam for heating buildings. In many chemical processes, where only a moderate temperature is required, and especially when inflammable substances are being dealt with, steam heating is used in preference to a fire or gas-flame, being safer and more easily controlled.

The feed-water for boilers is frequently heated by passing through a series of small pipes round which exhaust steam is circulated, thus saving a large quantity of heat which would otherwise be lost. A further effect of the heating of feed-water is to cause a precipitation of a portion of the salts of lime and magnesia held in solution, and special appliances are constructed for the double purpose of heating and softening the water prior to its being admitted to the boiler. The high latent heat of steam renders it extremely effective as a heating agent, the condensation of 1 lb. at 100° C. being sufficient to raise 5.37 lb. of water from the temperature of melting ice to the boiling-point.

Distillation.—A liquid containing solids in solution may be obtained pure by the process known as distillation. The liquid is boiled in a vessel known as a still, which is furnished with a widened portion at the top known as the still-head, on which a quantity of the vapour condenses and falls back into the still. The vapour which does not condense on the still-head is, in general, pure; and passes into a spiral tube or worm surrounded by running water, which cools and condenses the vapour. The purified liquid is collected at the end of the worm; and in this manner water or other liquids may be separated from solid matter.

The separation of two liquids, of different boiling points, may be effected by the employment of a more elaborate form of still-head. A simple distillation only will not suffice to separate two liquids completely, even though the boiling-points are considerably removed from each other, as partial evaporation takes place with all liquids at all temperatures. If, however, a succession of widened spaces be made in the still-head, which is elongated for this purpose, an almost complete separation can be effected. For example, the vapour reaching the first portion of the still-head might consist of equal parts of each constituent, and on condensing the latent heat of each would be disengaged. This latent heat would cause a certain amount of re-evaporation, and the mixed vapour thus produced would be richer in the constituent of lower boiling-point than the original mixture. This process of condensation and re-evaporation is repeated at every widened space in the still-head, the mixture becoming richer and richer in the lower boiling-point constituent, until on escaping it consists of this substance practically pure. The temperature at the entrance of the still head is that due to the mixture; at the exit it is the boiling-point of the pure liquid which escapes and is afterwards condensed.

In “patent” or Coffey stills for the production of pure alcohol by distillation from grain or other vegetable matter, a process of successive condensations and re-evaporations is carried out to separate the alcohol from the water which also evaporates from the mash. The still-head in this case consists of a chamber, in which perforated plates are placed at intervals, upon which the mixed vapours condense. Any liquid failing to re-evaporate falls through the perforations back into the still; and as alcohol has a lower boiling-point than water, the vapour between each successive pair of plates contains an increasing proportion of alcohol. If a sufficient number of plates be employed, the escaping vapour is practically pure alcohol, and is known as “silent” spirit, or spirit that does not indicate its origin, as small

quantities of distinctive substances, which would serve to show whether the alcohol had been derived from grain, are separated in the distilling process. These substances, which impart a flavouring to the alcohol, would not be separated by a less elaborate distillation.

At sea, fresh water is obtained from sea water by a process of distillation, the sea water being boiled by immersing in it a coil of piping through which high-pressure steam from the boilers is passed. In some recent forms of apparatus for this purpose a perforated metal plate is interposed between the still and condenser, which serves to intercept any spray or priming water that might be mechanically entangled in the steam, and which, if allowed to pass over, would impart a saline flavour to the water.

Condensers.—In steam-engines working with a condenser, the steam, after completing its work in the cylinder, is passed over a series of tubes through which water is flowing, and is thereby condensed. The condensed steam, being free from dissolved salts, is returned to the boiler, being preferable to ordinary water containing saline matter. At sea a condenser is essential, owing to the large quantity of salts present in sea-water, the condensation being effected by using sea-water to circulate through the condenser tubes. The special forms of condensers used in refrigerating machines are described in Chapter XVI.

Korting's Cooling Jets.—When water employed for cooling condensers is required to be used over and over again, to save the cost of a fresh supply, it is customary to cool the hot water escaping from the condenser by passing it through a specially-constructed jet, from which it escapes as a revolving spray. A large surface is thus exposed to evaporation, and the latent heat absorbed by the portion which evaporates is extracted from the residual water, which consequently undergoes a considerable fall in temperature. One gram of water at 80°C. , on evaporating, absorbs 551 calories, which, if extracted from 11 grams of water, initially at 80°C. , would reduce the temperature to 30°C. Korting's jets may be used with advantage whenever it is desired to cool a large mass of hot water rapidly.

CHAPTER XIV.

ATMOSPHERIC MOISTURE. HYGROMETRY.

Existence of Moisture in the Atmosphere.—The presence of water vapour in the atmosphere may be detected in many ways, as, for example, by exposing strong sulphuric acid or other hygroscopic substance, when an increase in weight, due to the absorption of moisture, will be noted after a time. By leading air through a tube surrounded by a freezing mixture, a quantity of water, extracted from the air, will be deposited. The water vapour present in the atmosphere is derived by evaporation from the surface of the sea and other masses of water, and is precipitated from time to time in the form of rain, snow or hail. The quantity of moisture present in a given quantity of air varies from day to day, and differs according to locality. The atmosphere is seldom saturated with water vapour, as a dish of water exposed to it almost invariably undergoes a diminution in weight. The normal condition of the moisture in the atmosphere is therefore that of an unsaturated vapour.

Effect of Temperature on Atmospheric Moisture.—As the quantity of vapour which can exist in a given space increases with the temperature, it follows that warm air can hold more moisture than cold air. At 10°C. , for example, 1 cubic metre of air can hold 9.3 grams of water vapour, whilst at 20°C. the amount required to produce saturation is 17.1 grams, and at 35°C. , 39.2 grams. Hence warm winds, which have travelled over the ocean—such as the S.W. winds in Britain—contain a much larger quantity of moisture than cold winds from the N. or E.

The maximum quantity of moisture that can be held by 1 cubic metre of air at different temperatures is shown graphically in Fig. 65. The ratio of the weights at two different temperatures is practically the same as the ratio of the saturation pressures. Thus at 12° and 24° , the ratio of the weights is $\frac{10.5}{21.4} = .49$; and of the saturation pressures $\frac{10.4}{22.1} = .47$. This approximate identity will be used later

in calculations concerning the condition of the atmosphere with respect to moisture.

Deposition of Moisture. Dew Point.—It has been stated that the atmosphere is seldom saturated with moisture, and on a given day, with a temperature of 25°C ., the actual amount of water vapour per cubic metre may be only 15 grams or less, whereas the quantity

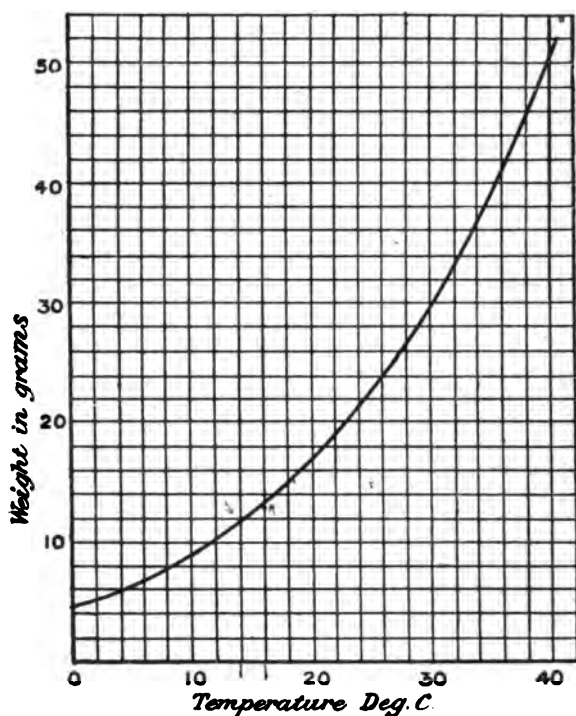


FIG. 65.—CURVE SHOWING WEIGHT OF WATER VAPOUR PRESENT IN 1 CUBIC METRE OF SATURATED AIR AT DIFFERENT TEMPERATURES.

would be 22·8 grams if the air were saturated. Assuming 15 grams to be present, and the temperature to fall, a point will be reached when the air, owing to its lessened power to hold moisture, will be saturated by the 15 grams present. Reference to the curve (Fig. 65) will show that saturation will occur at 18°C .; and if the temperature be lowered further, some of the moisture will be deposited. At 11°C . one cubic metre of air can only hold 10 grams of water vapour; hence if the temperature fell to 11° , a deposition of $(15 - 10)$

= 5 grams would ensue. In general, if moist air be cooled, a temperature will be reached at which deposition will commence. This temperature is called the dew point, and is obviously *the temperature at which the moisture present causes saturation*. It is evident that the dew point will vary according to the amount of water vapour existing in the atmosphere.

Hygrometric State or Relative Humidity.—It is customary to express the condition of the atmosphere with respect to moisture in the form of a ratio, which is termed the “hygrometric state” or “relative humidity,” which is defined as the ratio of the amount of moisture present in a given volume of air, to the amount required to saturate this volume at the existing temperature. Or,

Hygrometric State or Relative Humidity

$$= \frac{\text{Weight of water vapour present in unit volume of air}}{\text{Weight required to saturate unit volume at temp. of air}}.$$

A numerical example may be given to illustrate the definition. If it be found that 1 cubic metre of air at 25° C. contain 16 grams of water vapour, the hygrometric state will be $\frac{16}{22.8} = .70$, or 70 per cent., since 22.8 grams are required for saturation at 25° C. This method of expressing the result is apt to be misleading, as a higher hygrometric state may be associated with a less actual quantity of moisture. If at 15° C. the moisture present were 10 grams per cubic metre, the hygrometric state would be $\frac{10}{12.7} = .79$ or 79 per cent., although the actual amount is 6 grams less than in the previous case. The experimental determination of the hygrometric state may be carried out by the aid of instruments known as *hygrometers*, some forms of which will now be described.

The Chemical Hygrometer.—In this instrument a known volume of air is drawn through a series of drying-tubes, containing strong sulphuric acid or phosphorus pentoxide, which retain the moisture. The drying-tubes are accurately weighed before and after the experiment, the increase being the weight of water vapour in the known volume of air. In order to measure the quantity of air, a bottle of known capacity, fitted with an escape-tap at the lower portion, is filled with water and connected to the drying-tubes. The tap is then opened, and as the water escapes an equal volume of air is drawn through the tubes. The hygrometric state may be calculated from the increase in weight of the tubes, and a knowledge of the amount

required for saturation at the existing temperature, which may be obtained from tables or a curve similar to Fig. 65.

Example.—Five litres of air were drawn through drying-tubes, the observed increase in weight being $\cdot 073$ gram. Temperature of air = 22° C. To find the hygrometric state.

By definition, hyg. state

$$= \frac{\text{amount present in 5 litres}}{\text{amount required to saturate 5 litres at } 22^{\circ}}$$

From curve (Fig. 65) amount required to saturate 1 cubic metre, or 1000 litres at 22° = 19 grams. To saturate 5 litres $\frac{19}{200} = \cdot 095$ gm. will be required. Hence the hygrometric state is $\frac{\cdot 73}{\cdot 95} = \cdot 77$ or 77 per cent.

The chemical hygrometer is accurate, but tedious to use, as it is necessary to drag the air slowly through the tubes to ensure complete retention of the moisture. It is only employed practically when a very accurate result is desired.

Dines' Hygrometer.—The principle adopted in this and several other hygrometers is to ascertain the dew point, and also to note the temperature of the air, when the hygrometric state may be calculated by the use of a table of vapour pressures of water. Dines' hygrometer (Fig. 66) consists of an observation surface O, which may be

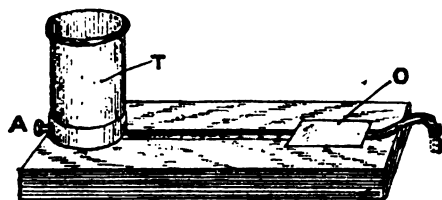


FIG. 66. —DINES' HYGROMETER.

cooled by iced water flowing on its under side from a tank T. The bulb of a thermometer, fixed horizontally, touches the under side of O, and the small chamber of which O is the cover is provided with an outlet for the water at its upper part. The rate at which the water flows may be controlled by a tap A. In conducting the experiment, the iced water is allowed to pass slowly through the chamber until a film of moisture is observed to form on the observation surface O, when the thermometer is read. The tap is then closed, and the temperature allowed to rise until the film of moisture vanishes, when a

second reading of the thermometer is taken. The mean of the two temperatures is taken as the dew point; thus if the film formed at 8.5° and disappeared at 9.5° , the dew point would be 9° . This means that the water vapour present would saturate the air if the temperature were 9° , and by noting the atmospheric temperature the hygrometric state may be determined by the ratio—

$$\frac{\text{Weight per unit volume required to saturate at dew point}}{\text{Weight per unit volume required to saturate at temperature of air}}$$

These quantities may be obtained from the curve in Fig. 65, or instead of taking weights, the ratio of the saturation pressures at the dew point and atmospheric temperature may be used, with a practically identical result.

Example.—To find the hygrometric state when the dew point is 9° C., and the temperature of the air 15° C. From the curve of weights required to saturate 1 cubic metre of air (Fig. 65) the amount corresponding to 9° C. is 8.8 grams, and to 15° C. 12.7 grams.

Hence the hygrometric state is $\frac{8.8}{12.7} = .69$, or 69 per cent. Or, taking saturation pressures from the table on page 216, the ratio becomes $\frac{8.57}{12.7} = .675$, or 67.5 per cent. The difference of 1.5 per cent. between the two results is well within the limits of error of the experiment.

In order to obtain a close result with Dines' hygrometer, several precautions must be taken. The observation surface should be made of a thin sheet of metal, a copper surface, lightly silvered, being the best for detecting the formation of the film of moisture. A thin piece of metal will also possess practically the same temperature on the under and upper surfaces, so that the thermometer will record the temperature of the air in contact with the upper surface—which is the temperature sought—nearly correctly. The instrument is frequently sold with a thick, black glass observation surface, when the formation of moisture is not only difficult to detect, but the temperature of the under surface, as recorded by the thermometer, may differ greatly from that of the upper surface, owing to the poor conductivity of glass, thus giving an erroneous value for the dew point. The water should be allowed to flow slowly, and should be stopped immediately the film is detected. If a thick layer of moisture be allowed to deposit, it will take a considerable time to evaporate, and give a false reading for the temperature of disappearance. The modification due to Professor Barrett, in which a second tank is provided, containing water

warmer than the air, enables a more certain reading of the temperature of disappearance to be taken, the procedure being to turn off the cold water immediately the film is observed, and then to turn on the warm water. This prevents a thick film from forming, and warms up the apparatus far more quickly than by allowing it to stand in air. A more sharply defined second reading is thus secured in a shorter time.

Daniell's Hygrometer.—This is another form of dew-point hygrometer, differing from the foregoing in the method of cooling the observation surface. Daniell's hygrometer (Fig. 67) consists of a tube furnished with a bulb at either end, and containing ether and ether vapour only, the air having been expelled by boiling before sealing up. A muslin cover is tied round one of the bulbs B, and the other bulb A is made of blackened glass, or has a band of gold leaf surrounding it to act as an observation surface.

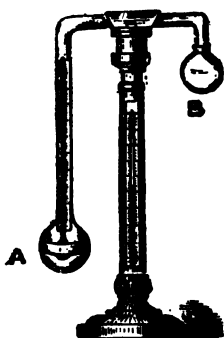


FIG. 67.—DANIELL'S
HYGROMETER.

A thermometer is placed in the portion of the tube connected with A, and serves to record the temperature of the ether in the latter. A second thermometer fixed to the stand, enables the temperature of the atmosphere to be read. In using the instrument, a volatile liquid is poured over B, where it is retained by the muslin. The evaporation of this liquid lowers the temperature of the bulb B, and causes the ether vapour in the interior to condense. This lowers the pressure on the surface of the liquid ether in the bulb A, which accordingly evaporates and by absorption of latent heat lowers the temperature of A and its contents. The evaporation of the ether in A, and the consequent fall of temperature, continue so long as B is cooled, and finally moisture makes its appearance on the surface of A. The temperature on the inner thermometer is noted when this occurs, and the apparatus is then allowed to warm up until the film disappears, when the inner thermometer is again read. As before, the mean of the two temperatures is taken as the dew point, and the hygrometric state calculated in the usual way.

The liquid generally used for external application to the bulb B is ether, which evaporates rapidly and so ensures the necessary cooling effect. Whilst Daniell's hygrometer is simple to use, some uncertainty must exist as to the accuracy with which the thermometer in A records the temperature of the outer surface of the bulb, that is, of the air at the moment it begins to part with its moisture.

Regnault's Hygrometer.—This hygrometer is shown in Fig. 68, and consists of two tubes, furnished with silver caps. One of the tubes is connected by a T-piece to an aspirator, and is partly filled with ether in which the bulb of a thermometer is immersed. The other tube contains air and does not communicate with the aspirator, its function being to furnish a comparison surface for the working-tube T, and to contain a thermometer which records the atmospheric temperature. The experiment is conducted by connecting the tube A to an aspirator, the result of which is to extract the air and ether vapour from the upper part of T, and to cause air to enter by the tube B and bubble through the ether. Each bubble of air becomes saturated with ether vapour, and the result of the evaporation is to cause a lowering of temperature in the residual ether. This is allowed to proceed until

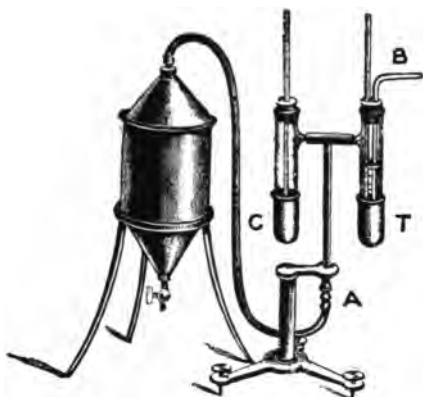


FIG. 68.—REGNAULT'S HYGROMETER.

moisture is observed to form on the silver cap on T, which then appears dimmer than the comparison surface on C. The aspirator is then stopped and the temperature at which the film disappears noted, judgment in this case also being aided by a comparison of the brightness of the two silver caps. The mean of the temperatures of appearance and disappearance, as usual, gives the dew point.

This instrument, if properly made, is the most accurate of the various forms of dew-point hygrometers. The rate at which the temperature falls can be completely controlled by the aspirator, and by cooling slowly near the dew-point a fine reading—to a fraction of a degree—may be obtained. The ether should be in actual contact with the silver cap, in which case the thermometer will correctly record the temperature of the outer surface of the silver, or very nearly so.

The advantages of Regnault's hygrometer are often nullified by the makers, who place the silver cap of the working-tube over a glass tube with a closed end, so that a layer of glass is interposed between the ether and the observation surface. This mistake is sometimes further aggravated by cementing the silver cap over the closed glass tube with plaster of Paris, thereby completely destroying the reliability of the indications.

The Wet and Dry Bulb Hygrometer.—All the hygrometers previously described require an experiment to be performed in order to obtain the hygrometric state, which, in the instrument under notice, is

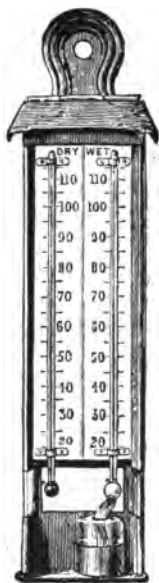


FIG. 69.—WET AND DRY BULB HYGROMETER.

deduced by the aid of tables from the readings of two thermometers. As shown in Fig. 69, this hygrometer consists of two similar thermometers, hanging side by side, the bulb of one thermometer being dry, and recording the atmospheric temperature, whilst the other bulb is kept wet by surrounding it with a piece of muslin connected to a wick immersed at its end in water. Owing to evaporation constantly taking place on the surface of the wet bulb, heat is extracted from the contained mercury, and consequently the wet-bulb thermometer shows a lower reading than the other, which is exposed to the atmosphere. If the air were saturated with moisture, no evaporation would occur, and in this case the two thermometers would read alike. On the other hand, if the atmosphere were very dry, rapid evaporation would take place on the surface of the wet bulb, and this thermometer would consequently indicate a much lower temperature than that of the atmosphere. Between these two extremes, the difference between the two readings will vary according to the amount of moisture present, which determines the rate of evaporation.

Numerous attempts have been made to establish a simple formula by the aid of which the hygrometric state might be deduced from the two readings, but without success. It has been found possible, however, to compile tables from which the desired result may be obtained, the figures in the tables having been arrived at as a result of daily comparisons between the readings of the wet and dry bulb thermometers and a dew-point hygrometer. These daily observations were conducted in several countries, and were extended over a number of years, so as to embrace a very large variety of atmospheric con-

ditions. The results obtained are embodied in the following table, in a form convenient for calculating the hygrometric state.

In the table the first column, headed "t° C.," represents the

THE WET AND DRY BULB HYGROMETER.

t° C.	0	1	2	3	4	5	6	7	8	9	10
0	4·6	3·7	2·9	2·1	1·3
1	4·9	4·1	3·2	2·4	1·6
2	5·3	4·4	3·6	2·7	1·9	1·1	0·3
3	5·7	4·8	3·9	3·1	2·2	1·4	0·6
4	6·1	5·2	4·3	3·4	2·6	1·8	0·9
5	6·5	5·6	4·7	3·8	2·9	2·1	1·2
6	7·0	6·0	5·1	4·2	3·3	2·4	1·6
7	7·5	6·5	5·5	4·6	3·7	2·8	1·9	1·1	0·2
8	8·0	7·0	6·0	5·0	4·1	3·2	2·3	1·4	0·6
9	8·6	7·5	6·5	5·5	4·5	3·6	2·7	1·8	0·9
10	9·2	8·1	7·0	6·0	5·0	4·0	3·1	2·2	1·3
11	9·8	8·7	7·6	6·5	5·5	4·5	3·5	2·6	1·7
12	10·5	9·3	8·2	7·1	6·0	5·0	4·0	3·0	2·1	1·2	0·3
13	11·2	10·0	8·9	7·6	6·5	5·5	4·5	3·5	2·5	1·6	0·7
14	11·9	10·7	9·4	8·3	7·1	6·1	5·0	4·0	3·0	2·0	1·1
15	12·7	11·4	10·1	9·0	7·8	6·6	5·5	4·5	3·4	2·5	1·5
16	13·5	12·2	10·9	9·7	8·4	7·3	6·0	5·0	4·0	3·0	1·9
17	14·4	13·0	11·7	10·4	9·1	8·0	6·7	5·6	4·5	3·5	2·4
18	15·4	13·9	12·5	11·2	9·9	8·6	7·4	6·3	5·1	4·0	3·0
19	16·3	14·9	13·4	12·0	10·7	9·4	8·1	6·9	5·7	4·6	3·5
20	17·4	15·9	14·3	12·9	11·5	10·2	8·8	7·6	6·4	5·2	4·1
21	18·5	16·9	15·3	13·8	12·4	11·0	9·6	8·4	7·1	5·9	4·7
22	19·7	18·0	16·4	14·8	13·3	11·9	10·5	9·1	7·8	6·6	5·4
23	20·9	19·2	17·5	15·9	14·3	12·8	11·3	10·0	8·6	7·3	6·1
24	22·2	20·4	18·6	17·0	15·3	13·8	12·3	10·9	9·4	8·1	6·8
25	23·5	21·7	19·9	18·1	16·4	14·8	13·3	11·8	10·3	9·0	7·6
26	25·0	23·1	21·1	19·4	17·6	15·9	14·3	12·8	11·3	9·8	8·4
27	26·5	24·5	22·5	20·7	18·8	17·1	15·4	13·8	12·3	10·8	9·3
28	28·1	26·0	24·0	22·0	20·1	18·3	16·6	14·9	13·3	11·8	10·2
29	29·8	27·6	25·5	23·5	21·5	19·6	17·8	16·1	14·4	12·8	11·2
30	31·5	29·3	27·1	25·0	22·9	21·0	19·1	17·3	15·5	13·9	12·3

temperature of the atmosphere, as recorded by the dry bulb, whilst the figures under the columns headed 0, 1, 2, 3, etc., give the vapour pressure at the dew point corresponding to differences of 0, 1, 2, 3, etc., degrees C. between the wet and dry bulb readings. Taking the dry bulb reading as 21° C., and the wet bulb 18° C., the difference is 3° , and to find the hygrometric state, the figure opposite 21° in the column headed "0" is divided into the figure opposite 21, in the column headed "3." The hygrometric state is, therefore, $\frac{13.8}{18.5} = .75$ or 75 per cent. The column headed "0" is identical with a table of saturation pressures, and if the two bulbs showed the same reading at any temperature, the difference would be 0, and the hygrometric state 100 per cent. Further examples in the use of the table are appended.

Example 1.—The dry bulb temperature being 16° C., and the wet bulb 12° C., to find the hygrometric state and also the dew point.

Difference between readings = $(16 - 12) = 4$.

Vapour pressure at dew point, obtained from column 4, in horizontal row opposite $16^{\circ} = 8.4$ mm.

Saturation pressure at 16° C., from column 0 = 13.5 mm.

Hygrometric state = $\frac{8.4}{13.5} = .62$ or 62 per cent.

As the vapour pressure at the dew point is 8.4 mm., the dew point must be the temperature at which the saturation pressure equals 8.4 mm. Looking for the figure 8.4 in the column headed 0, or in a table of vapour pressures of water, it is seen that this value obtains between 8° and 9° , the figures for which are 8.0 and 8.6 mm. respectively. The dew point would, therefore, be 8.6° C. approximately.

Example 2.—To find the hygrometric state and dew point corresponding to readings of 24.5° on the dry bulb, and 20.2 on the wet bulb.

The table only gives values for whole degrees, but proportionate parts may be taken for fractions of a degree. The saturation pressure at 24.5 may be taken as intermediate between the values at 24° and 25° , or $\frac{22.2 + 23.5}{2} = 22.85$ mm. The difference between the readings is 4.3° . Under column 4, opposite 24° , the figure is 15.3 mm., and under column 5, 13.8 mm. The proportionate value for 4.3° is, therefore, 14.85 mm. Similarly, in the row opposite 25° C., the figure under column 4 is 16.4 , and under 5 is 14.8 ; whence the proportionate value for 4.3° is 15.92 mm. The value for 24.5° ,

with a difference of 4.3° , is, therefore, $\frac{14.85 + 15.92}{2} = 15.37$ mm.

Hence the hygrometric state is $\frac{15.37}{22.85} = .67$ or 67 per cent. The dew point, or temperature at which 15.37 mm. represents saturation pressure, is seen from column o to be 17.8°C .

It will be seen from the latter example that when fractions of a degree are involved, the calculation is somewhat complicated. For the use of unskilled observers approximate tables have been compiled, which assume that the thermometers are only read to the nearest $\frac{1}{2}^{\circ}\text{C}$. or whole degree F. The results obtained are sufficiently close for ordinary purposes.

When in use, the wet and dry bulb hygrometer should be freely exposed to air, but should be kept in the shade. The dish of water should be well removed from the dry bulb, and the cover of the wet bulb washed or renewed periodically, as it tends to become choked with dust. Owing to the ease with which readings may be taken, this hygrometer is far more extensively used than other types, which are only employed for precise readings.

Hygrosopes, or Moisture Indicators.—Many appliances are in use designed to indicate, rather than measure, the relative humidity of the atmosphere. Some varieties of sea-weed, and other forms of vegetation, absorb moisture from a damp atmosphere, which evaporates again on the air becoming dry, thus enabling an indication to be obtained from the condition of the plant. A paper soaked in a solution of cobalt chloride is pink when damp, and blue when dry, and furnishes, by its colour changes, a guide to the state of the atmosphere with respect to moisture. A human hair, free from grease, contracts in length on absorbing moisture, and in the atmosphere will either increase or decrease in length according to the variations in the proportion of water vapour present. Hygrosopes based on the alteration in length of hair have been devised by De Saussure, Monnier, and others, in which the movements of the hair are communicated to an index hand, behind which a dial is placed. The scale on the dial is usually marked to read directly the percentage of relative humidity, but the readings are at best only approximate. The most recent form of this type of hygroscope is Lambrecht's polymeter (Fig. 70). The dial, over which the index connected to the hair moves, is furnished with two scales, one of which is gradu-

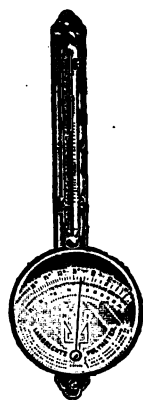


FIG. 70.
LAMBRECHT'S
POLYMER.

ated so as to give the hygrometric state directly, whilst the second scale is divided in such a manner that the figure opposite the index, when subtracted from the reading of the thermometer placed above, gives the dew point. The attached thermometer is graduated in ordinary degrees on one side, whilst on the other side saturation pressures are marked opposite corresponding temperatures. Instead of using a single hair to move the index, a number of hairs are fastened together so as to form a single strand, greater strength being thus secured. Lambrecht's polymeter is one of the most suitable instruments to use when approximate readings only are required. Other forms of direct-reading hygrosopes have been based on the alteration in length of whipcord, catgut, and other materials, under varying conditions of atmospheric moisture.

Uses of Hygrometric Observations.—Daily observations of the hygrometric state of the atmosphere are made at meteorological stations, and assist in obtaining a forecast of the weather; thus a generally dry condition of the atmosphere over the country would indicate the probable absence of rain, and *vice versa*. A series of observations would also serve to indicate whether the climate of a place were generally damp or otherwise, and so furnish a clue as to its desirability for residential purposes. The existence of abnormal dampness in a house or building can be detected by hygrometers, or even by hygrosopes, such observations being of value from a hygienic standpoint. In weaving delicate fabrics a certain minimum of atmospheric moisture is essential, as in a dry atmosphere the strands would become brittle and snap, consequently the atmosphere is artificially moistened by steaming when the normal hygrometric state is too low. The dangers attendant on the manufacture of gunpowder, and of explosives and ammunition generally, are greater in a dry than in a moist atmosphere, hence in factories where explosives are handled it is arranged that the hygrometric state shall not fall below a certain minimum, and the same applies to storage magazines for explosive materials. In horticulture, hygrometers are employed to register the percentage of moisture in the atmosphere of greenhouses, so that a deficiency may be detected and remedied by sprinkling with water. The allowance for evaporation to be made in constructing a large water reservoir depends in part upon the average hygrometric state of the atmosphere in the locality, the evaporation being greater in a dry atmosphere.

Dew.—On clear nights, when radiation can take place freely from the surface of the earth, the temperature of the ground falls considerably. When this occurs to such an extent that the ground and objects

near it sink in temperature below the dew point of the air near the surface, the surplus moisture is deposited in the form of globules on the various objects. Moisture so deposited is called dew, and if the temperature should fall still further, until the freezing point is reached, the dew freezes and forms hoar frost. Most of the moisture which goes to form dew rises in the form of vapour from the porous ground. This may be proved by placing a metal vessel—such as a dish-cover—on the ground, mouth downwards, on a suitable night, when, on examination in the early morning, the deposit of dew will be found in the interior of the vessel. If the moisture had condensed from the atmosphere itself, the dew would have formed on the exterior of the vessel. Owing to the evaporation of underground water, vapour is continuously rising from porous ground, and on a cold night is condensed on the nearest objects on reaching the surface. Sometimes, however, ordinary atmospheric moisture is also deposited, as the roofs of houses may often be observed to be covered with moisture or hoar frost.

Mists and Fogs.—The condensation of moisture in the atmosphere itself results in the formation of small spheres of water, which, owing to their small size, and the consequent large surface in comparison with mass, remain floating for a considerable time in the air. The ratio of the surface exposed to friction to the mass is very large in a tiny sphere, and although the density of liquid water is 770 times that of air, the friction suffices to hold very small globules in suspension. When the atmosphere is charged with these small spheres of water, the appearance is known as a mist or fog. The cloud resulting from the escape of a jet of steam into air is similarly constituted.

It has been shown by Aitken that each little sphere of water contains a speck of dust in the centre round which the moisture has condensed, and that in the absence of dust a mist could not form. When a jet of steam is led into dust-free air no cloud is formed, and condensation only occurs when the steam comes into contact with cold, solid matter, such as the sides of the vessel containing dust-free air. An obvious analogy is here suggested to the phenomena of surfusion and abnormal boiling, as in each case external aid is necessary to initiate the change of state. So small a nucleus is required to enable water vapour to liquefy, that the excessively minute particles known as “electrons” are capable of effecting the condensation.

Mists are generally confined to a region near the surface, and are caused by the cooling effect of the ground on the atmosphere, the result being that the adjacent air is cooled below the dew-point, and the surplus moisture settles on the particles of dust always present.

Hence mists may generally be observed over moist land on cool evenings, the vertical extent being determined by the height to which the atmosphere is affected by the cold surface. In fogs, on the other hand, a general cooling of the atmosphere occurs, probably due to a gentle admixture of cold air, the excess of moisture again being deposited round dust nuclei. A fog may extend to a vertical height of several hundred feet, and it sometimes happens that during a fog the ground is warmer than the overlying air, thus indicating a different origin to that of a mist. In large cities where the atmosphere is laden with smoke particles, a yellowish-brown colour, due to the smoke, generally accompanies the fog, and adds greatly to the density. This colour is usually associated with London fogs, the atmosphere being laden with smoke particles from factories and domestic chimneys, and dust caused by the enormous street traffic. The hygro-metric state of the atmosphere in London is generally fairly high, and thus the whole conditions favour the formation of dense fogs. The still condition of the atmosphere which usually accompanies a high barometer is favourable to foggy weather ; a strong wind causing the fog to disperse by absorbing the condensed moisture.

Various attempts have been made to devise a method for dissipating fogs, so as to obtain clear spaces in localities where traffic is otherwise practically suspended, as, for example, the mouths of harbours, railway stations, and busy street crossings. Amongst the methods tried mention may be made of the blowing of warm, dry air through trumpet-shaped openings, over the locality, so as to evaporate the moisture ; and of the electrical method, in which the air and spheres of water are electrified by proximity to wires carrying a current at high potential, when the small spheres cohere, forming drops which rapidly fall to the ground. None of the methods proposed have yet passed the experimental stage.

The intensity, and probably the number, of fogs occurring in large centres of population would undoubtedly be lessened if the smoke in the atmosphere were reduced to a minimum, either by the perfecting of smoke-prevention appliances for industrial and domestic fires, or by the general use of smokeless fuel. The inconvenience and financial loss entailed by a dense fog, render persistent efforts in this direction highly desirable.

Clouds and Rain.—Clouds represent masses of condensed water vapour, floating in the atmosphere at a height varying from 10 miles downwards. As in the case of mists and fogs, the individual globules of water composing the cloud are formed round dust-centres. The condensation originates in a cooling effect produced by currents of

cold air mingling with warmer and moister air. As clouds are denser than the atmosphere a continuous sinking takes place, and if a dry region of the atmosphere be entered, the condensed water will again become vapour, and the cloud disappear. If a cloud enters a moister region, or if the initial cooling be great, larger spheres of water form, which are not able to float in the air, and fall as rain. The size of the water globules is the only distinction between a Scotch mist, in which the particles are small and sink slowly, and a heavy rain, which is due to large particles falling rapidly. The freezing of the smaller type of spheres produces snow, whilst hail represents large globules which have solidified after formation.

The amount of rain which falls in a district during a given time is measured by means of the *rain-gauge*, which is a cylindrical vessel into which a funnel is placed. The diameter of the funnel-top is accurately known, and the rain falling within it runs into the cylinder, from which it is transferred to a measuring vessel. The result is expressed in inches of rainfall, that is, the depth to which water would have formed from the rain on a non-porous surface. By employing a narrow measuring-cylinder, fractions may be obtained ; thus if the area of the top of the funnel were ten times that of the bore of the measure, an actual fall of $\frac{1}{10}$ th of an inch would fill the measure to a height of 1 inch, and a very small fall could thus be measured. The rainfall of a district depends upon the nature of the prevailing winds, the presence of elevated masses of land, and other causes. A knowledge of the average annual rainfall of a district is essential to the engineer when deciding upon a locality for a surface water-supply ; and is of the highest importance from an agricultural standpoint.

CHAPTER XV.

THE PRODUCTION OF LOW TEMPERATURES. LIQUEFACTION OF GASES.

Methods by which Low Temperatures may be Obtained.—A reduction of temperature may be obtained by means of the following processes :—

1. The solution of a solid in a liquid, or the mutual liquefaction of two solids. This method has been dealt with in Chapter IX. under the head of freezing mixtures.

2. The evaporation of a liquid, when conducted without the application of external heat.

3. The expansion of a compressed gas, when work is done during the expansion.

4. The escape of a compressed gas through a fine opening or jet.

All these methods have been usefully applied, and those not hitherto described will furnish the subject matter of the present chapter.

Production of Low Temperatures by the Evaporation of Liquids.—The rapid evaporation of a liquid is usually procured by applying heat, in which case the latent heat of vaporisation is furnished by the flame or other source of heat. If, however, the liquid be made to evaporate rapidly by mechanical means, such as the reduction of the pressure on its surface, the latent heat will be extracted from the liquid itself, and to some extent from the containing vessel, the result being a fall of temperature. Rapid evaporation is necessary to obtain a considerable lowering of temperature, as the latent heat extracted in a given time then greatly exceeds the heat received by the liquid from surrounding objects. A vessel of water, exposed to air, shows practically no fall in temperature, because the evaporation proceeds so slowly that the latent heat absorbed is balanced by the gain from the atmosphere and surrounding objects. When allowed to evaporate under the receiver of an air-pump, however, the heat which enters the water from without is far less, in a given time, than that which disappears in the form of latent heat, and consequently a notable fall in temperature occurs.

As in the case of freezing mixtures, a definite limit of low temperature exists for a given liquid undergoing evaporation. This limit is reached when the latent heat extracted from the liquid is equal to the heat entering from without. Even if it were possible perfectly to shield a liquid from external heat, a stage would be arrived at when the pump would fail to maintain a less pressure in the space than the existing vapour pressure, when evaporation would cease and no further fall in temperature could take place. The vapour pressure of liquids diminishes as the temperature falls, and finally obtains a value as low as the vacuum-producing power of the pump, which then ceases to be operative. As an example, the case of water in a flask, originally at $20^{\circ}\text{C}.$, and connected to an air-pump may be considered. On reducing the pressure to 17.4 mm. (which is the pressure of water vapour at $20^{\circ}\text{C}.$), the water will boil, and as every gram which evaporates at $20^{\circ}\text{C}.$ absorbs 592.6 calories from the residual liquid and vessel, the temperature will fall, and the vapour pressure also. When $0^{\circ}\text{C}.$ is reached, the vapour pressure is only 4.6 mm., and as a less number of vapour molecules suffice to furnish the diminished pressure, the rate of evaporation falls off considerably. The rate of evaporation may be taken roughly as proportional to the pressure; hence at $0^{\circ}\text{C}.$ the vapour formed in a given time is $\frac{4.6}{17.4}$, or roughly $\frac{1}{4}$ of that given off at $20^{\circ}\text{C}.$ At $0^{\circ}\text{C}.$ the water freezes, and any further cooling is due to vapour leaving the ice. At $-20^{\circ}\text{C}.$ the pressure falls to $.93$ mm., and the rate of evaporation to $\frac{.93}{17.4}$, or roughly $\frac{1}{20}$ of the original rate. With the best available appliances a further reduction of temperature would not be found possible, as it would be necessary to maintain a higher degree of vacuum than $.93$ mm., and to shield the vessel so perfectly that the minute extraction of latent heat resulting from the feeble evaporation would overcome the ingress of heat from surrounding objects. When these opposing tendencies are balanced, the limit of low temperature is reached.

It is evident from the foregoing that a liquid capable of maintaining a high vapour pressure, even at low temperatures, or which gives rise to a solid possessing a high vapour pressure, is better suited than water for obtaining low temperatures. Ether, for example, has a vapour pressure of 69 mm. at $-20^{\circ}\text{C}.$, and if the limit of the pump were 1 mm. internal pressure, it is evident that a much lower temperature than $-20^{\circ}\text{C}.$ could be obtained by the use of this liquid. In general the more volatile the liquid, the greater will be the reduction of temperature attainable. The most volatile liquids are those obtain-

able by the condensation of gases, and consequently the study of methods for producing low temperatures is intimately associated with that of the liquefaction of gases, which will now be entered into.

Liquefaction of Gases by Pressure.—In 1806 Northmore discovered that chlorine gas on being subjected to pressure, undergoes liquefaction; this being the first recorded instance of a gas being made to assume the liquid state. At 12.5° the pressure required is 8.5 atmospheres, and at 0° , 6 atmospheres. At -34° C. chlorine liquefies under a pressure of 1 atmosphere. Some years later Faraday continued the investigation, and showed that many gases could be liquefied easily by combined cooling and pressure. Faraday took a stout glass tube, sealed at both ends, chemicals for the generation of the gas under experiment being placed in one end of the tube, whilst the free end was surrounded by a freezing-mixture. By liberating a large amount of gas in the closed tube, a high internal pressure was produced, which, combined with the cooling, brought about liquefaction. In this way Faraday liquefied sulphur dioxide, carbon dioxide, nitrous oxide, cyanogen, ammonia, and hydrochloric acid; and also investigated the properties of the liquids obtained.

The pressure required to produce liquefaction is equal to the vapour pressure of the liquid at the existing temperature. Thus sulphur dioxide, which liquefies at -8° C., under 1 atmosphere pressure, possesses a vapour pressure of 1 atmosphere or 760 mm. at this temperature, which is therefore the normal boiling-point of the liquid. At 0° C. the vapour pressure rises to 1165 mm., and if a closed bottle contain liquid sulphur dioxide at 0° C., the internal pressure will be 1165 mm. Hence the reason why cooling facilitates liquefaction: the vapour pressure of the liquid, and consequently the pressure required to cause liquefaction, are lowered.

The following table shows the vapour-pressures of a number of gases at 0° C.

Name	Vapour Pressure in Atmospheres	Name	Vapour Pressure in Atmospheres.
Sulphur dioxide .	1.53	{ Sulphuretted hy- drogen }	10.00
Cyanogen . .	2.37	Hydrochloric acid.	26.20
Ammonia . .	4.40	Nitrous oxide .	32.00
Chlorine . .	5.95	Carbon dioxide .	38.50

The superiority of any of these liquids over water or ether in respect to the production of low temperatures by evaporation is made

evident by the above figures. Under the receiver of an air-pump a temperature below -50°C. can easily be obtained with liquid sulphur dioxide, as the amount of evaporation is still considerable. When the pressure on any liquefied gas is liberated, boiling commences, and as the latent heat of vaporisation is extracted from the liquid itself, the temperature falls to the boiling point of the liquid at the reduced pressure. Thus when exposed to the atmosphere, liquid sulphur dioxide acquires a temperature of -8°C. ; ammonia, -33.7°C. ; and carbon dioxide -78.2°C. This fall of temperature to the normal boiling point is identical with the case of water under pressure in a steam boiler, which falls in temperature to 100°C. when the boiler is fully opened to the atmosphere.

Most liquid gases can be caused to solidify by placing under the receiver of an air-pump, and rapidly exhausting the contents. The solidification of carbon dioxide may be easily brought about by filling a steel cylinder, tubed after the manner of a soda-water syphon, with the liquid; when, on opening the valve, the liquid is driven by the internal pressure through the tube, escaping into the atmosphere in the form of a spray. The rapid evaporation of the globules composing the spray, combined with the cooling effect due to the escaping gas doing work in overcoming the atmospheric pressure, causes so low a temperature that the inner portions of the globules solidify, forming a finely-divided white powder. By tying a flannel bag, two or three layers thick, over the exit-tube, the solid may be collected and its properties examined. The solid evaporates in air without previous liquefaction, its temperature being about -90°C. Rapid evaporation of the solid in a vacuum causes the temperature to fall to -120°C. , or even lower, the vapour pressure of the solid being noticeable even at this temperature.

The gases hydrogen, nitrogen, oxygen, air, and carbon monoxide baffled all the attempts of the early experimenters to reduce these substances to the liquid state, in spite of the application of enormous pressures and the best available means of cooling. The term "permanent gases" was applied to distinguish these gases from others which could be liquefied, and it was thought by some investigators that a distinction existed between the so-called "permanent" gases and others, which rendered the liquefaction of the former class impossible. The researches of Andrews, however (published in 1869) threw a new light on the problem, and by indicating the conditions necessary to produce liquefaction, ultimately led to the condensation of all the "permanent" gases. Andrews discovered that a temperature exists for every gas below which no amount of pressure will cause

liquefaction, to which the term "critical" temperature was applied. Above 31°C. , for example, carbon dioxide cannot be obtained in the liquid state, no matter what pressure be exerted. The explanation of the failure to liquefy hydrogen, oxygen, and other gases was that the critical temperatures were so low that ordinary cooling failed to reach them, and consequently the application of high pressures was of no avail. Later work has completely demonstrated the truth of this proposition; but before describing the means adopted for the condensation of the gases difficult to liquefy, it will be advantageous to consider the important conclusions to which the researches of Andrews lead.

Critical Temperature. Continuity of Liquid and Gaseous States.—Assuming that a liquid differs from a gas in the respect that the molecules tend to cohere, owing to a lessened velocity and closer proximity, the existence of a critical temperature indicates that nearness alone, as produced by pressure, does not give rise to sufficient cohesive power to enable the properties of a liquid to be manifested. In addition to being closer together, the speed at which the molecules move must not exceed a definite rate, and the critical temperature is that at which the molecular velocity is just small enough to permit of the necessary cohesion. It might be inferred from this that the liquid and gaseous states are not abruptly separated, but that every intermediate state between liquid and gas may exist. Andrews showed that this actually was the case, and that these two conditions of matter—liquid and gaseous—merge insensibly into one another.

A well-defined liquid differs from a gas or vapour physically in that it possesses a greater density, a higher refractive index, a less amount of internal energy—shown by the absorption of heat on vaporising—and in possessing a boundary surface or meniscus. The consideration of the case of water, heated in a closed boiler, will serve to show that these distinctions are only relative. As the temperature rises, the number of vapour molecules in the space above the water increases rapidly, and therefore the density of the steam becomes greater. At 100°C. the density of the steam is only $\frac{1}{1700}$ of that of the water, but at 230° the value has risen to $\frac{1}{80}$, and above this temperature shows a rapidly augmented increase. At the same time the density of the water diminishes, owing to expansion; and evidently a stage will be reached at which liquid and vapour possess the same density. The same reasoning applies to the index of refraction; and as the temperature rises the energy absorbed in the act of evaporation becomes less and less, finally becoming zero when

the molecules of the liquid attain the same velocity as those of the vapour. The boundary surface, or meniscus, possessed by a liquid is due to surface tension, which causes the surface to assume a curved shape. The value of the surface tension falls as the temperature rises, the meniscus becoming flatter or less curved, and finally becomes zero, at which stage the bounding surface disappears, and the liquid becomes vapour. All the distinctions enumerated between a liquid and its vapour cease to hold at a certain temperature, which is the critical temperature of the substance. This temperature for water is $365^{\circ}\text{C}.$, at which steam and water have the same density and refractive index; and at which temperature also the latent heat of vaporisation and surface tension have zero values. As all these properties change gradually, it follows that the transition from liquid to vapour, and *vice versa*, is continuous, and not abrupt.

The behaviour of a gas at different temperatures, ranging on either side of the critical temperature, may be studied with advantage by reference to the isothermals in Fig. 71, which represent the results obtained by Andrews for carbon dioxide.

Starting with the lowest isothermal (the temperature being steady at $13^{\circ}\cdot 1$ throughout, whilst the pressure was varied), and proceeding from the right-hand side, it will be observed that at first the volume diminishes and the pressure rises. At about 50 atmospheres, however, the pressure remains steady, whilst the volume diminishes, the isothermal becoming parallel to the axis of volumes. During the stage represented by the horizontal line, liquefaction has taken place, and as the pressure of a vapour in contact with its liquid is constant for a given temperature, a further diminution in volume merely causes more

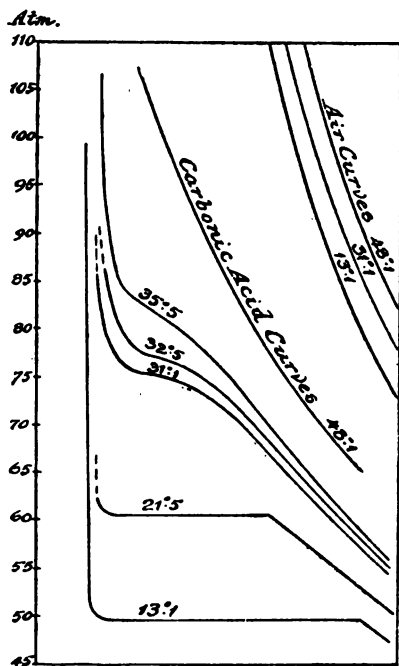


FIG. 71.—ISOTHERMS OF CARBON DIOXIDE (Andrews).

vapour to liquefy, without altering the pressure. When the whole of the gas has been liquefied, the pressure is applied to the liquid only, and as liquids in general are only slightly compressible, a rise in pressure to 90 atmospheres or more causes little decrease in volume, as shown by the vertical part of the isothermal. The next isothermal, for 21.5°C ., shows the same general features; no liquefaction commencing, however, until a pressure of 60 atmospheres has been applied. The third isothermal, representing pressure and volume changes at 31.1°C ., has no horizontal portion, although a flexure in the curve occurs at 75 atmospheres; and the absence of the horizontal part implies that the vapour was not in contact with its liquid, or, in other words, no liquid was formed—which in the experiment was observed to be the case. In the isothermals for 32.5° and 35.5° the flexure is still present, but less marked, and at 48.1° has entirely disappeared, when the shape approximates to that of the rectangular hyperbola which represents Boyle's law. The limiting case, when the isothermal just ceases to show a horizontal part, occurs at 30.92°C ., which is the critical temperature of carbon dioxide.

Critical Pressure.—The pressure required to produce liquefaction at the critical temperature is known as the critical pressure. In a diagram such as Fig. 71, the critical pressure would be represented by the mark opposite the horizontal portion of the critical temperature isothermal. The term does not apply to any other isothermal; and if that for carbon dioxide at 30.92 were drawn, the horizontal part would be opposite 73 atmospheres on the pressure scale. Hence 73 atmospheres is the critical pressure of carbon dioxide. A table of critical temperatures and pressures is appended :—

Name	Critical Temperature, Degrees C.	Critical Pressure, Atmospheres
Carbon dioxide	30.92	73
Sulphur dioxide	156	79
Alcohol	243	63
Ether	194	35.6
Ammonia	130	115
Water	365	196
Oxygen	-118	50
Nitrogen	-146	34
Hydrogen	-240	15.4

Pictet's Liquefaction of Oxygen.—In 1877, Pictet, of Geneva, succeeded in liquefying oxygen by cooling the gas, under a high pressure, to a temperature which proved to be below the critical temperature, now known to be -118°C . The oxygen was compressed into a steel tube, furnished with a tap, and cooled by means of a jacket of liquid carbon dioxide, which was exhausted by a pump. Finally, on opening the tap, a pale blue liquid was seen to escape, which evaporated almost instantaneously. It was thus demonstrated that the possibility of reducing gases such as oxygen to the liquid state depended, as predicted by Andrews, upon the production of a temperature below the critical temperature of the gas.

Cailliet's Liquefaction of Oxygen.—By an independent method, Cailliet succeeded in liquefying oxygen in the same year as Pictet. The principle adopted was the cooling effect obtained when a gas is allowed to expand suddenly from a high pressure, doing work during the expansion. The gas was compressed into a thick-walled glass tube by means of a hydraulic press, and cooled by means of solid carbon dioxide or a liquefied gas. On opening a valve connected to the press, an outlet was afforded for the contents; the gas therefore expanded suddenly, driving out the water, and consequently falling in temperature. By employing high pressures it was found that the cooling effect was sufficient to cause liquefaction, the liquid being visible in the form of globules on the sides of the tube. In order to prevent the gas becoming wet, mercury was used in the lower half of the cylinder of the press, the result of the pumping being to drive the mercury up the tube containing the gas, and so to reduce the volume to any desired extent.

Siemens' Regenerative System for Producing Low Temperatures.—About the year 1862 Sir William Siemens devised a method for obtaining low temperatures, based on the cooling effect observed when a gas at high pressure escapes through a jet into the atmosphere. The actual fall of temperature noted by Joule and Kelvin for air (see Chapter VI.) was 29°C . per atmosphere difference of pressure on the two sides of the jet, hence air at 0°C . and 101 atmospheres pressure, escaping through a jet into a space at 1 atmosphere pressure, would fall in temperature by 29°C . Siemens proposed to utilise this effect for producing indefinitely low temperatures, by allowing the gas escaping through the jet to play upon a metal spiral through which the gas passed before reaching the jet. The principle of the method is illustrated in Fig. 72, which shows a metal spiral terminating in a fine jet, and connected at the other end to a supply of gas at high pressure. The gas on leaving the jet is cooled, and by impinging on

the spiral lowers the temperature of the interior gas which is about to escape. Each portion leaving the jet is consequently cooler than the preceding portion, and if the apparatus could be well shielded from external heat, it would appear that the temperature would continue to fall indefinitely. The principle involved is the exact converse of that utilised for the production of high temperatures in the Siemens' regenerative furnace. Although the process is in reality continuous, it may perhaps be simpler to understand by considering different stages. Thus if at the commencement the air were at 10°C ., and the pressure such as to cause a fall of 10° in the escaping gas, the latter would

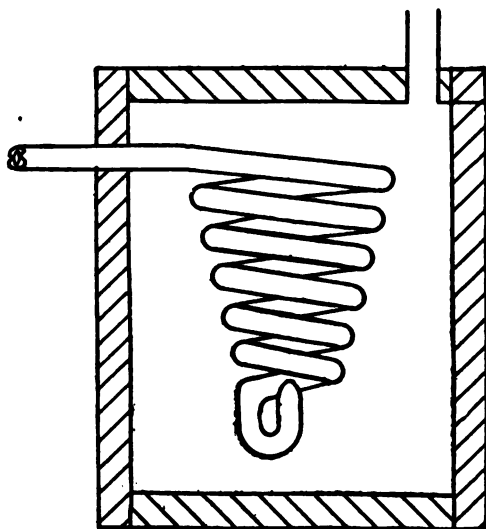


FIG. 72.—PRINCIPLE OF SIEMENS' REGENERATIVE METHOD FOR PRODUCING LOW TEMPERATURES.

be at 0°C . on leaving the jet. By circulating round the spiral the cold air would eventually reduce the temperature of the gas about to escape to 0°C ., and if the same pressure were maintained, the temperature after escape would be -10°C ., and so on. Siemens does not appear to have applied the system practically, but its revival by Linde, Dewar, and others has resulted in the liquefaction of all known gases, with the single exception of helium, and has enabled large quantities of liquid air, oxygen, nitrogen, hydrogen, etc. to be obtained readily. It is found that at low temperatures the cooling effect is much greater, for the same difference of pressure, than at atmospheric temperatures, which adds further to the efficiency of the process.

Linde's Apparatus for Liquefying Air.—The liquefaction of air was accomplished by Dr. Linde in 1895 by means of the regenerative system, the method of cooling the gas approaching the outlet being more effectual, however, than that suggested by Siemens. The arrangement employed is shown in Fig. 73, and consisted of a compressor C, by means of which air was driven through a cooling-tank T, the heat of compression being removed by circulating water round the pipe through which the air passed. After leaving the cooler, the air was passed through the inner tube of a double spiral S, into a vessel V through a small valve A, which could be regulated to produce any desired size of opening. After undergoing cooling by expanding

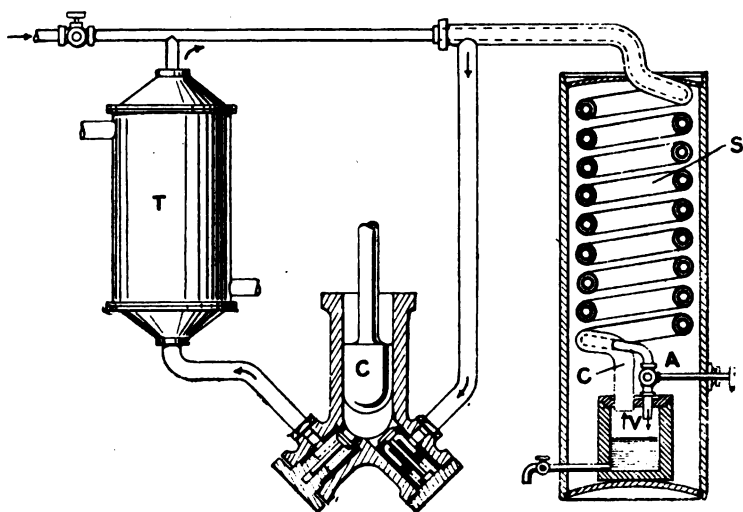


FIG. 73.—LINDE'S APPARATUS FOR LIQUEFYING AIR (early form).

from the valve, the air escaped from the vessel V through the outer tube C, thus completely surrounding the oncoming gas contained in the inner tube, and effectively reducing its temperature. Finally, the air again entered the compressor, and was again forced round the circuit. After the lapse of 15 hours liquid air began to collect in the vessel.

In the modern forms of machines for the production of liquid air the same principle is applied, but by improvements in the working parts the liquefaction can be accomplished in a much shorter time. Machines of this type have been devised by Linde, Hampson, and others. In Dewar's apparatus for the rapid production of liquid air

a steel cylinder containing air at 200 atmospheres pressure is connected to a copper coil which is surrounded by solid carbon dioxide, which serves to cool the air to about -80°C . The air, after traversing this coil, passes on to a second coil, furnished with a pin-hole outlet, and surrounded by a vacuum vessel. After a few minutes liquid air escapes through the pin-hole, and collects in the vessel.

Liquefaction of Hydrogen.—Prof. Dewar was the first to accomplish the liquefaction of hydrogen in 1898, although Olszewski and others had previously obtained a froth partly composed of the liquid. The hydrogen, at a pressure of 180 atmospheres, was passed through a spiral surrounded by liquid air, and afterwards expanded through

a spiral terminating in a fine jet, and contained in a vacuum vessel. Considerable quantities of the liquid were thus collected; and by connecting the vessel to an air-pump and exhausting, the solid was readily obtained. Solid air and nitrogen may also be obtained by exhausting the respective liquids; but owing to possessing a low vapour pressure, liquid oxygen fails to solidify when treated in this manner.

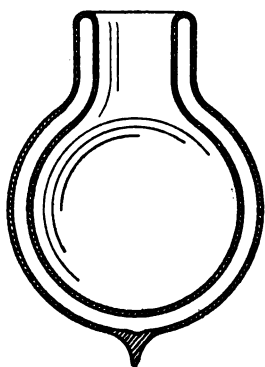


FIG. 74.—DEWAR'S VACUUM VESSEL.

Collection of Liquid Gases. Dewar's Vacuum Vessel.—The preservation of liquefied gases at very low temperatures presented considerable difficulties to the early investigators, it being found impossible to insulate the collecting vessel so

perfectly as to prevent rapid evaporation. An arrangement of three glass vessels, separated by air spaces—resembling a nest of three beakers—was the appliance commonly used until Dewar introduced the vacuum vessel. This consists of two separate glass vessels, sealed together at the neck, and separated by a vacuum. Fig. 74 shows a section of Dewar's vessel, which is remarkable from the perfection with which a substance placed in the inner compartment is shielded from the ingress of heat. The complete removal of the air forms a space almost entirely free from conduction and convection, and by silvering the interior of the outer vessel, radiant heat is almost entirely prevented from entering. Any external heat reaching the contents must pass by conduction down the sides of the inner vessel, and as glass is a bad conductor of heat, the amount entering in a given time is extremely small. The superiority of the vacuum over any other form of insulation is so marked, however, that the

absence of gaseous conduction and convection would not appear to furnish a complete explanation. One litre of liquid air, for example, may be kept in a vacuum vessel for 24 hours without entirely evaporating, although the atmospheric temperature would be 200° C. higher than that of the liquid air. If boiling water be poured into a Dewar vessel of about 1 pint capacity, and the neck be closed by a cork, a temperature of about 90° C. will be indicated after the lapse of 12 hours. A protected Dewar vessel is now sold for the use of travellers and sportsmen under the name of the "Thermos" bottle, by the aid of which food may be kept hot for a long period. When used to store liquefied gases, the neck is plugged with cotton wool, so as to permit of the free escape of the gas given off by the liquid.

Low Temperature Data.—The following figures have been determined for liquefied gases, the temperatures being measured by a gas thermometer, a thermal junction, or a platinum resistance thermometer:—

Substance	Boiling Point, Degrees C.	Freezing Point, Degrees C.
Nitrous oxide	-143	-150.5
Oxygen	-182.5	-238
Nitrogen	-193	-214
Hydrogen	-252.5	-257

Lowest Temperature yet Attained.—If solid hydrogen be caused to evaporate under the receiver of an air-pump, a temperature of -262° C., or even lower may be attained. The limit of cooling is reached when the vapour pressure of the hydrogen becomes comparatively small. It is possible, however, to attain a still lower temperature by the use of the rare gas helium, which up to the present has not been liquefied. Dewar, and more recently Olszewski, have attempted to liquefy helium by compressing the gas in a glass tube, and afterwards allowing it to expand suddenly, the apparatus devised by Cailletet for the liquefaction of oxygen being used. Before expansion the helium was cooled with solid hydrogen to below -250° C., and on expanding from 180 atmospheres to 1 the temperature fell to -271.3° C. This is the lowest temperature yet attained, being only 1.7° C. removed from absolute zero; but is still insufficient to cause helium to liquefy. If sufficient helium could be

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collected to use in a regenerative apparatus, after a preliminary cooling with solid hydrogen, its liquefaction would no doubt be effected, and by the rapid evaporation of the liquid or solid, a closer approximation to absolute zero could be obtained.

Properties of Matter at very low Temperatures.—The properties of different kinds of matter are profoundly modified at very low temperatures, such as that of liquid air. Many organic substances, such as feathers, become phosphorescent when cooled in liquid air; and substances normally soft become frozen into hard, brittle solids. A piece of beef or other flesh, and vegetable matters also, become so brittle that they may be ground up to powder in a mortar. Mercury freezes to a hard solid, which, if pointed, may be driven into wood with a hammer. Metals in general, when cooled to the temperature of liquid air, exhibit a great increase in tensile strength, which, in the case of steel, is to some extent permanent after the steel has regained the normal atmospheric temperature. The resistance offered to electricity by metals also shows a great diminution, so much so that the resistance would appear to vanish—or nearly so—at absolute zero. Substances in general offer an easier passage to heat at very low temperatures, this fact explaining, in part, the reason why a vacuum jacket is so immeasurably superior to a lagging for protecting liquid gases from external heat. Chemical actions which take place with violence at ordinary temperatures cannot be made to operate at the temperature of liquid air; the combination of liquid hydrogen with fluorine being the solitary exception to the general suspension of chemical activity. These, and many other striking phenomena, serve to show the extent to which the properties of matter, as we know them, depend upon the heat energy present.

Uses of Liquefied Gases.—A number of liquefied gases are now used for commercial purposes, and may be obtained from the makers stored in steel cylinders, in which the substance retains the liquid form owing to its own vapour pressure. Amongst these may be mentioned nitrous oxide, or laughing gas, which is used in mild operations to produce unconsciousness; chlorine, for use in certain metallurgical processes, such as the refining of gold; and sulphur dioxide, used for disinfecting and other purposes. The advantage gained by storing these gases in the liquid form is that the inconvenience of preparation is avoided, and a large quantity is condensed into a small space. Liquid carbon dioxide is largely used in the manufacture of aerated waters; and on the small scale water may be aerated in syphons by inserting a small steel cylinder, filled with liquid carbon dioxide, and known as a “Sparklet,” in the neck of the

syphon, and liberating the contents by piercing the cylinder : when a large volume of gas is produced which saturates the water, and provides sufficient pressure to discharge the contents when the tap is opened. Liquid carbon dioxide, ammonia, and sulphur dioxide are also used in refrigerating machinery.

At present liquid air, although it may be manufactured fairly cheaply, has not been applied successfully to any industrial process. Attempts have been made to use this liquid for propelling the motor of a vehicle, but the cost of production is too great to enable a liquid air motor to compete with one in which fuel or electricity is employed. A possible future use for liquid air may be found in the treatment of steel, which has been found by Hadfield to be permanently improved by dipping in this liquid. As the cost of production becomes less, many uses for liquid air will no doubt be found.

Many experiments have been made with a view to utilising liquefied gases as propelling agents in guns, whereby the corrosive action of the hot gases produced by an explosive would be avoided, and the propelling force generated less suddenly. In no case, however, has complete success been attained.

Liquefaction of Helium.—By passing helium through a spiral cooled with frozen hydrogen, and allowing the escaping gas to cool the spiral further, as described on page 270, Professor Onnes, of Leyden, has succeeded in liquefying helium. The solid was obtained by evaporating the liquid under reduced pressure. The liquefaction temperature was found to be about -269°C. , and the freezing-point a little lower ; it is evident, therefore, that the figures given by Dewar and Olszewski (p. 273) to represent the temperatures obtained in their attempts to liquefy helium were incorrect. Every known gas has now been reduced to the liquid and solid condition.

CHAPTER XVI.

REFRIGERATING MACHINERY; ICE MANUFACTURE;
AND COLD STORAGE.

Objects of Commercial Refrigeration.—In industrial processes involving refrigeration, such as the preservation of food and perishable articles, the cooling of liquids such as water and milk, the manufacture of ice, and the cooling of rooms, it is not desired to obtain an excessively low temperature, but rather to produce and maintain indefinitely a moderately low temperature. Many food-stuffs would be seriously damaged if made too cold, and the difference between successful and unsuccessful preservation frequently depends upon the maintenance of a temperature not varying by more than two or three degrees Centigrade. A refrigerating machine, therefore, should be capable not only of producing the low temperature desired, but should permit of complete regulation of the cooling action, in order that this temperature may be kept practically constant. Modern refrigerating machinery enables both these ends to be secured, and has rendered possible the safe transport of perishable foods from the most distant parts of the globe. It is probably correct to state that no invention, in so short a time, has proved of more general service to mankind than the refrigerating machine.

Early Forms of Refrigerating Machines. Carré's Ice Machine.—Mechanical refrigeration may be said to have originated in the experiments of Dr. William Cullen, who, about the year 1755, discovered that a compressed gas was cooled by expansion. Cullen also discovered that water could be frozen by evaporation in a vacuum, and constructed a machine which consisted of an air-pump and receiver, in which the water to be frozen was placed. The least leakage in the air-pump, however, caused the process to fail; and under the best conditions, the operation of freezing the water was tedious. No advance on the discoveries of Cullen was made until the year 1810, when Leslie showed that if a quantity of strong sulphuric acid were present in the receiver of the air-pump, the water could be frozen much more rapidly, as the water vapour was absorbed by the acid as

quickly as it formed, thus maintaining a vacuum chemically, and not relying upon the mechanical removal of the vapour from the pump. For many years the attempts at mechanical refrigeration proceeded in the direction of producing ice by the evaporation of water, assisted by a chemical absorbent; and in 1850 E. Carré, of Paris, invented a machine which was capable of producing a small quantity of ice in a few minutes, and which was largely used in hotels and restaurants. Carré's machine, which is still used to some extent, consisted of an air-pump of special construction, worked by hand, to which a vessel containing the water to be frozen was attached. In the interior of the pump, a chamber was placed containing strong sulphuric acid which assisted the action of the pump by absorbing the water vapour. In order to prevent the formation of a water-saturated layer on the surface of the acid, a stirring device was arranged, so that at every stroke of the pump the acid was agitated, and a fresh surface exposed for absorption. The acid required frequent renewal, and could easily be removed from the machine for this purpose.

The great drawback to the use of Carré's machine, and to the method in general, is the necessity of maintaining a vacuum of less pressure than 4·6 mm. of mercury, or about $\frac{1}{8}$ of a pound per square inch. This represents the vapour pressure of water at the freezing-point, and unless a pressure smaller than 4·6 mm. be maintained in the vessel, evaporation will cease, and with it the cooling effect. The least wear on the plunger of the pump will cause sufficient leakage to prevent this degree of vacuity being attained, and consequently no ice will be formed. The introduction of the Fleuss pump, with oil-sealed valves, has largely overcome this difficulty, and many types of machine for producing small quantities of ice on this principle are now on the market, in which the superior type of pump is used and which are consequently more certain in action than Carré's machine. An attempt to apply the method on a large scale was made by Windhausen in 1870, but the ice produced proved to be frothy in character, and as such commanded no market; and in addition, the process gave trouble from the difficulty of maintaining a proper vacuum. The necessity of renewing the sulphuric acid is a further drawback to the use of these machines, which are now only used for the production of ice on the small scale.

Principles of Modern Refrigerating Machinery.—Three distinct systems are in use at the present time for producing a cooling effect by mechanical or other means, which may be classified as under.

1. *Air Expansion System.*—The principle of this system is the cooling-effect produced by the expansion of a compressed gas, dis-

covered by Cullen about the year 1755. As shown in Chapter VI., the extent of the cooling depends upon the work done during the expansion, and in machines of this type the expanding gas is allowed to do work usefully by helping to compress the next charge. Atmospheric air is employed in all machines working on this system, being cheaper than any other gas, and equally efficient.

2. *The Compression System.*—In this case a gas or vapour is liquefied by pressure in a coil of piping surrounded by cold water. It is then passed on to a second coil, surrounded by the medium it is desired to cool, and there allowed to evaporate. The latent heat of evaporation is extracted from the medium surrounding the coil, which thereby undergoes a lowering of temperature.

3. *The Absorption System.*—A strong solution of ammonia gas in water is heated, the gas being thereby expelled, and by conducting the operation in a closed space, the pressure exerted by the liberated gas causes it to liquefy, and to collect in a cool receiver connected with the space. The liquefied gas is then allowed to evaporate, and thus to cool its surroundings; after which it is absorbed in cold water or weak solution of ammonia, thus forming a strong solution from which it is again expelled by heat, and the previous operations repeated. The absorption system differs from the compression system only in the manner in which the liquefaction of the gas is effected.

The special features of machines based upon each system, together with the advantages and drawbacks, will now be entered into.

Air-Expansion Machines.—The first successful application of the cooling effect produced by the expansion of compressed air was made by Dr. Gorrie, of Florida, U.S.A., in 1845. Air was compressed in a cylinder, into which a jet of water was injected, which served to absorb most of the heat of compression. After being further cooled by passing through a chamber surrounded by cold water, the compressed air was allowed to expand in a cylinder into which a jet of salt water was forced. The cooling due to the expansion caused the salt water to fall considerably in temperature, and the cold brine thus obtained was drawn off and circulated round vessels containing water, which ultimately froze. Improvements on this machine were made by Windhausen, Kirk, Bell, Coleman and others, resulting in the standard types of machine now manufactured.

Air-expansion machines are now made to work on the "open cycle," in which case the expanded and cooled air is discharged directly into a cold store; or on the "closed cycle," in which the cooled air is allowed to circulate round coils or vessels containing the

liquid to be cooled, and afterwards returned to the compressor. The general arrangement is shown in Fig. 75, in which C represents the compression cylinder, E the expansion cylinder, and D the cooler. The charge of air is compressed in C to a pressure sufficient to lift the valve communicating with D. The hot compressed air then passes through the cooler D, which consists of a series of tubes over which

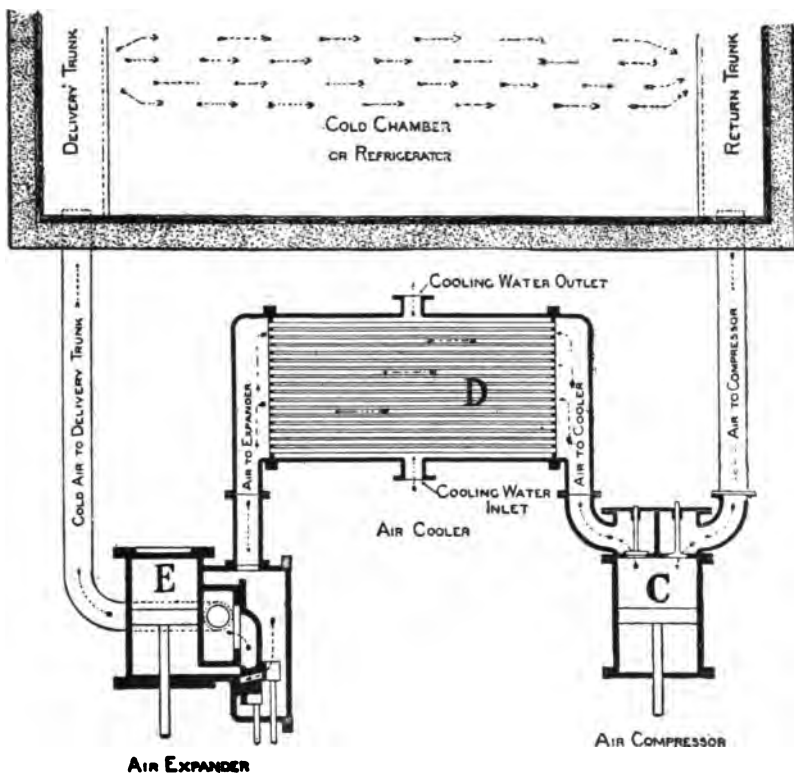


FIG. 75.—PRINCIPLE OF AIR-EXPANSION REFRIGERATING MACHINE.

cold water is caused to flow continuously. The cooled charge, still under high pressure, passes into the expansion cylinder E, the piston of which is connected to the same shaft as that of the compressor. The compressed air, by driving down the piston of E, does work in assisting to turn the shaft, thus compressing another charge in C; hence the expansion is accompanied by a considerable reduction in temperature. On the return stroke of the piston in E, the cold air is dis-

charged through a pipe into the cold store or other space. When the piston in C is on the down stroke, a valve communicating with the opposite side of the cold store opens downwards, thus allowing a partly-cooled charge to enter, which is again compressed, cooled, expanded, and delivered into the cold chamber. By this means, the whole of the air in the chamber is cooled down to the desired temperature. It is evident that the pistons of C and E must be coupled to the shaft in such a manner that compression in the former and expansion in the latter occur simultaneously; that is, the up stroke in C corresponds to the down stroke in E, and *vice versa*. The delivery of cold air from E to the chamber will then correspond to the entrance of a fresh charge from the chamber into C.

Air-expansion machines may be driven by a steam engine or motor coupled directly on to the shaft of the machine, or by means of a belt from independent shafting. Fig. 76 represents an air expansion machine manufactured by the Haslam Foundry and Engineering Company, of Derby, driven by steam. The steam engine is compound, with the two cylinders arranged tandem, and is shown to the right in the illustration. The compressor is worked by the middle crank, and the expander coupled to the crank to the left. The cooler is placed at the back of the machine, which is thus compact and self-contained. Where vertical space is a consideration, a horizontal type of machine is used.

Advantages and Drawbacks of Air-Expansion Machines.—The chief point in favour of air-expansion machines is the cheapness and accessibility of the medium, no re-charging being necessary after repairs as in the case of machines of other types. There is no danger to the attendant, moreover, in case of leakage, whereas such media as ammonia and sulphur dioxide are highly dangerous. The extent of the cooling can be regulated by slowing down the engine, or by controlling the amount of the compression by means of the valves.

A great drawback is the amount of space occupied, for a given refrigerating capacity, compared with machines of the compression type. Trouble also arises from the accumulation of snow, due to the freezing of water vapour in the air, in the expander. A snow-box is placed in the pipe communicating with the cold chamber in which the snow so formed collects, and is removed periodically, failing which the pipe might become choked. Another device is to cool the compressed air, before admission to the expander, by circulating round it cold air from the chamber on its way to the compressor, whereby most of the moisture is deposited as liquid, and may be drained off.

In either case the necessity of removing the moisture entails a complication of the machinery.

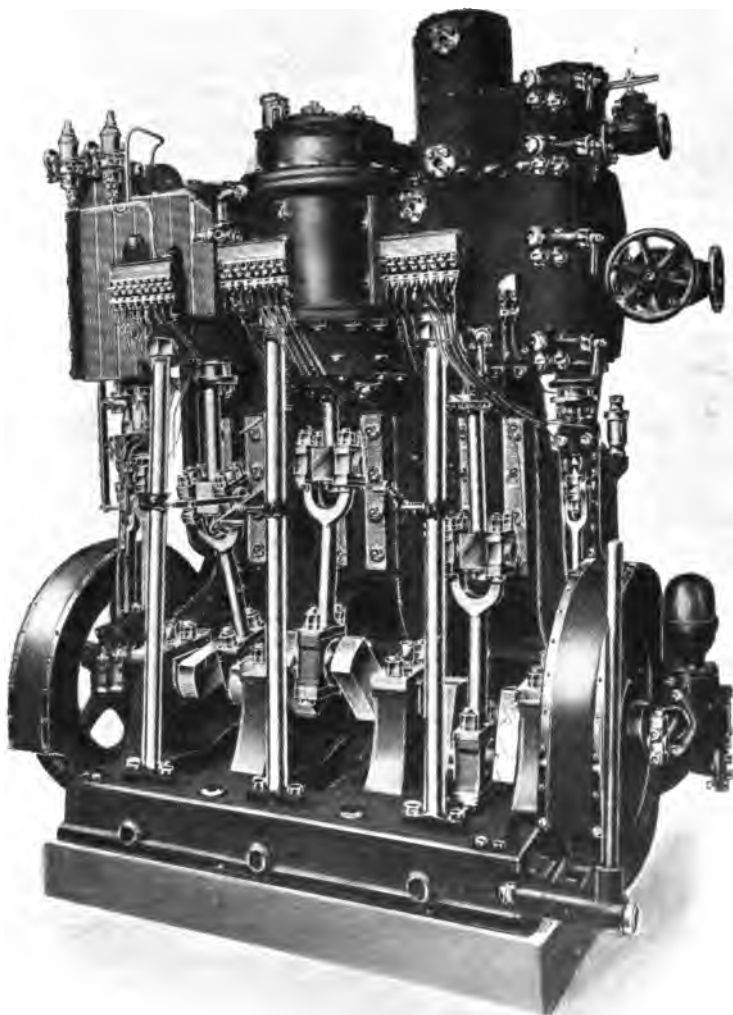


FIG. 76.—STEAM-DRIVEN AIR-EXPANSION REFRIGERATING MACHINE.

Another serious drawback is the low efficiency of air-expansion machines compared with those of other types, due in large measure to

the low temperature attained by the expanded air. It will be shown later that the highest efficiency of any type of machine is secured when the medium is cooled to the minimum extent consistent with proper refrigeration. It is far more economical, for example, to circulate 100 cubic feet of air cooled by 50° , than 50 cubic feet of air cooled 100° . Limitations of size in the machines render it necessary to circulate a comparatively small volume of air, intensely cooled, in order to secure the desired reduction in temperature, and as a result the efficiency is low. For a given expenditure of horse-power in driving the machines, a compression machine will give 4 or 5 times the refrigerating effect of an air-expansion machine. For this reason the compression type of machine has now almost entirely superseded the air-expansion machine, even on boats carrying large cargoes of perishable food, the difficulty of renewal of the medium being overcome by carrying reserve supplies in the liquid form, stored in cylinders.

The principles governing the efficiency of refrigerating machines in general are dealt with in detail in Chapter XX., and may with advantage be studied in connection with the present chapter.

The Compression System.—The first attempt to apply the liquefaction and subsequent evaporation of a substance to practical refrigeration was made in 1834 by Jacob Perkins, who experimented with a volatile liquid derived from the distillation of rubber. The vapour produced by subjecting this liquid to a reduced pressure was compressed, re-forming the liquid, which was then allowed to evaporate in a space surrounded by the substance to be cooled, from which the latent heat of vaporisation of the liquid was extracted. The resulting vapour returned to the compressor, to be again liquefied and sent to the evaporator; the heat produced by the liquefaction in the compressor being removed by cooling-water. Perkins did not succeed in producing a commercial machine, but his experiments demonstrated the possibility of obtaining a continuous refrigerating effect by subjecting a condensable vapour to a proper cycle of operations. It was not until 1860, however, that the process was employed for industrial purposes, when James Harrison, of New South Wales, revived the project, and by using ether as medium succeeded in constructing a machine which at once came into use for ice manufacture and other purposes. The introduction of ammonia as the medium by Linde in 1873 marked the next great step in the development of compression machines, and was followed in 1876 by the employment of sulphur-dioxide by Pictet, and of carbon-dioxide by Raydt in 1881. Since the last date great improvements in the design and details of com-

pression machines have been made by various inventors, with the result that, except for special purposes, other types are now seldom constructed.

The cycle of operations in a modern compression machine may be understood by reference to Fig. 77. Assuming the interior of the machine to be fully charged with the medium, the upward stroke of the piston compresses the gas in the cylinder, and, at a given pressure, causes a valve connected with the condenser to open. The condenser consists of a coil of piping round which cold water is circulated, the heat produced by the compression being thus removed. The pressure employed suffices to liquefy the gas, which condenses in the coils, and is pushed forward through a regulating valve into a second set of coils, surrounded by the liquid to be cooled. The downward stroke of the piston causes a diminution of pressure in the cylinder, when the valve connected with the refrigerator or evaporator coils opens, the liquid in these coils then evaporating and entering the cylinder; the valve communicating with the condenser being closed meanwhile owing to the superior pressure behind it. The cooling effect is due to the latent heat of vaporisation of the liquid, which is extracted from the evaporator coil and its surroundings. A separator is interposed between the cylinder and condenser coil, which serves to intercept any lubricating oil which may be carried over from the cylinder, and which, if not removed, would finally choke up the coils.

It is evident that the foregoing set of operations is repeated at every double stroke of the piston, and hence the cooling effect is continuous. The act of compression represents the conversion of work into heat, which is removed by the cooling-water; the act of expansion represents the conversion of heat—derived from the substance to be cooled—into work, which is utilised in the back stroke of the piston in helping to drive the machine. Heat is taken in at one side and rejected at the other, but, in direct opposition to the action of a heat engine, the heat is rejected at the higher temperature and taken in at the lower. A refrigerating machine in reality is the converse of a heat engine in respect to the cycle of operations. In a refrigerating machine the medium enters the cylinder at the lower temperature and leaves at a higher, work being absorbed in the process, whilst in a heat engine the medium enters at the higher temperature and leaves at the lower, work being given out as the result.

The general arrangement of parts in an actual machine is shown in Fig. 78, which is self-explanatory. A point which calls for comment is the different readings of pressure recorded on the two gauges,

one of which is connected to the condenser and the other to the evaporator coils, in spite of the fact that both coils communicate. The explanation is to be found in the small size of the opening

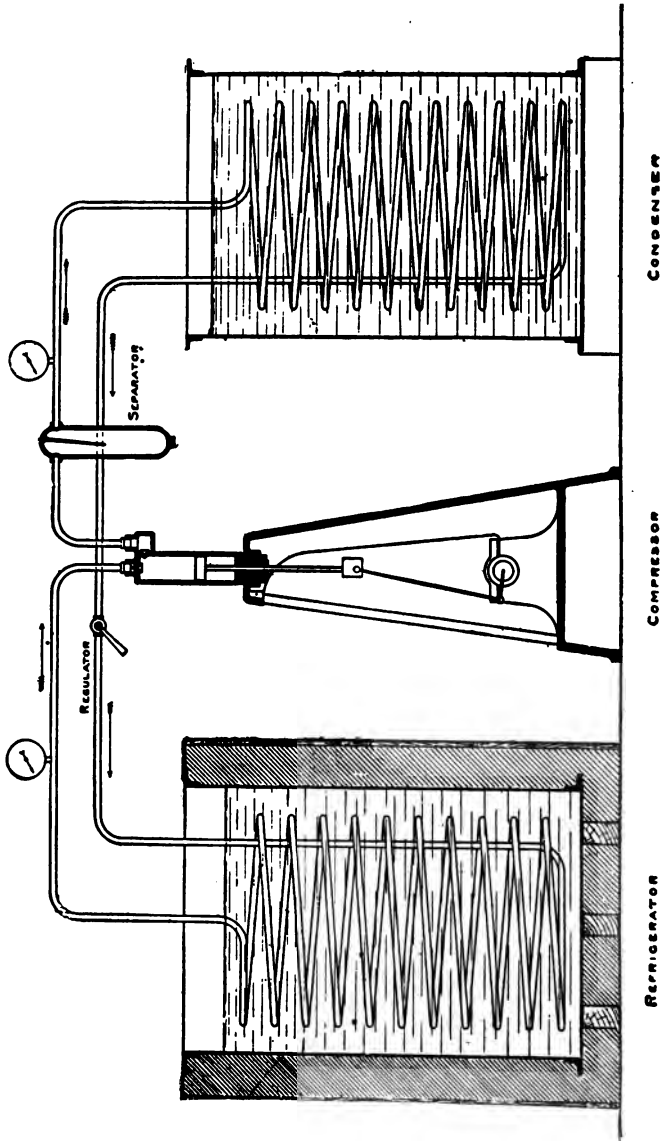


FIG. 77.—PRINCIPLE OF COMPRESSION SYSTEM FOR REFRIGERATING MACHINES.

connecting the two sets of coils, which can be varied in dimensions by the regulator. If a wide opening connect two vessels containing a gas, the pressure in both vessels will be the same ; but if only a tiny orifice be provided it is possible to maintain widely different pressures in the two vessels. Hence, owing to the small opening connecting the two sets of coils, a higher pressure may exist in the condenser than in the evaporator.

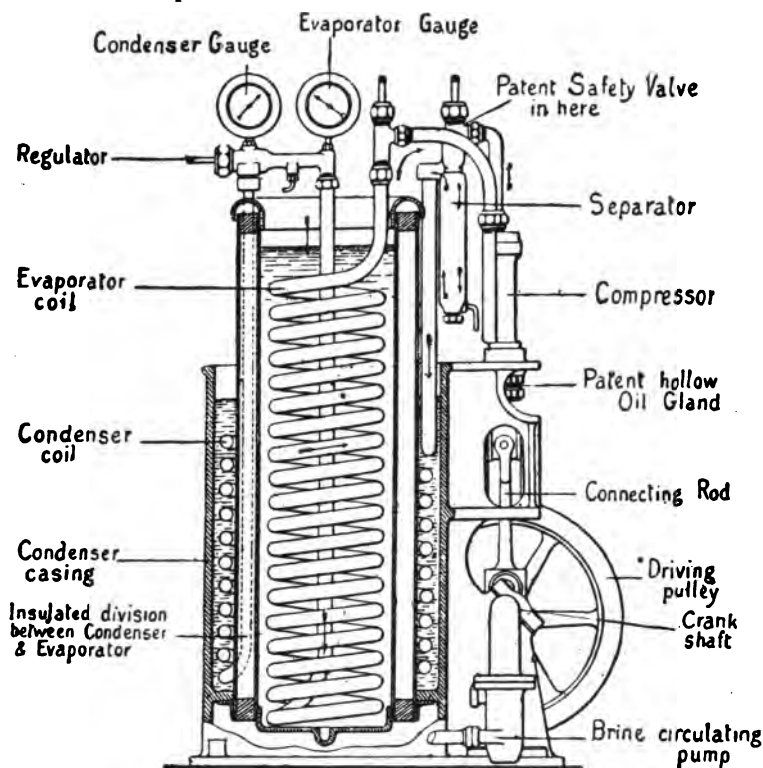


FIG. 78.—ARRANGEMENT OF PARTS IN COMPRESSION MACHINE.

Choice of Medium.—Theoretically, as the medium used serves merely to carry the heat, any gas or vapour fulfilling the conditions imposed should be as efficient as any other. In practice, however, the chemical and physical peculiarities of the gas or vapour selected must be taken into account. Obviously, a gas which corrodes the working parts would be inadmissible, and it is further desirable to use a non-inflammable medium, in order that leakage may not be accom-

panied by the danger of explosion. General use has only been made up to the present of ammonia, carbon-dioxide and sulphur-dioxide; ether being more rarely used on account of its extreme inflammability. The relative fitness of the three gases named will now be separately considered.

Ammonia gas (NH_3) is extremely cheap, and may be liquefied by the application of moderate pressures at ordinary atmospheric temperatures. It possesses a high critical temperature, viz. 130°C . or 266°F ., and may therefore be liquefied by pressure under any existing atmospheric conditions. The liquid has a high latent heat of vaporisation, and both gas and liquid have no chemical action on iron or steel. On the other hand, copper and its alloys (brass, bronze, etc.) are seriously corroded by ammonia, and cannot be employed in any part of the machine to which the gas has access. Further, ammonia gas is extremely poisonous, and a considerable leakage may prove fatal to the operator. A small leakage is readily detected by the pungent odour of the gas. In modern machines a dangerous leakage is a somewhat remote contingency, and the favourable properties of the gas in other respects have caused ammonia to be extensively used in compression machines. A table is appended showing the constants of ammonia at different temperatures.

In connection with the table on p. 287, it should be remembered that gauge pressure is less than absolute pressure by 14.7 lb. per square inch. The pressure required to ensure liquefaction at any given temperature may be obtained from the table—thus at 100°F . the absolute pressure requisite is 215.12 lb. per square inch, or 14.6 atmospheres. This pressure would therefore exist in the condenser coils when the temperature inside—always higher than that of the cooling-water outside—is 100°F . The diminishing value of the latent heat of vaporisation as the temperature rises is common to all liquids, the value becoming zero, as has previously been pointed out, at the critical temperature.

Carbon-dioxide (CO_2) is cheaper even than ammonia, and has the valuable property, both in the gaseous and liquid states, of being chemically inert towards all ordinary metals, thus affording a wider choice in materials for constructing the machine than when ammonia is used. Carbon-dioxide is not specifically poisonous, although an atmosphere of the gas will not sustain animal life. The escape of an entire charge from a machine into the engine room is unaccompanied by any dangerous results, the percentage of oxygen in the atmosphere not being reduced sufficiently to give rise to risk of suffocation. In these respects carbon-dioxide is superior to ammonia as a refrigerating

CONSTANTS OF AMMONIA (NH_3).

Specific heat of ammonia vapour—Constant pressure . . . = 0.508
 „ „ „ Constant volume . . . = 0.3913
 „ ammonia liquid . . . = 1.01235 + 0.008378 t

Temperature Degrees F.	Gauge Pressure. lb. per sq. in.	Latent Heat of Evaporation. B.Th.U. per lb.	Volume of 1 lb. in Cubic Feet		Weight of 1 cubic foot in Pounds	
			Vapour	Liquid	Vapour	Liquid
-30	-0.57	573.69	18.69	.0237	.0535	42.123
-25	+1.47	570.68	16.44	.0238	.0608	41.858
-20	3.75	567.67	14.51	.0240	.0690	41.615
-15	6.29	564.64	12.83	.0241	.0779	41.374
-10	9.10	561.61	11.38	.0243	.0878	41.135
-5	12.22	558.56	10.12	.0244	.0988	40.900
zero	15.67	555.50	9.03	.0246	.1107	40.650
+5	19.46	552.43	8.07	.0247	.1240	40.404
10	23.64	549.35	7.23	.0249	.1383	40.160
15	28.24	546.26	6.49	.0250	.1541	39.920
20	33.25	543.15	5.84	.0252	.1711	39.682
25	38.73	540.03	5.27	.0253	.1897	39.432
30	44.72	536.91	4.76	.0255	.2099	39.200
35	51.22	533.78	4.31	.0256	.2318	38.940
40	58.29	530.63	3.91	.0258	.2554	38.684
45	65.96	527.47	3.56	.0260	.2809	38.461
50	74.26	524.30	3.24	.0261	.3084	38.226
55	83.22	521.12	2.96	.0263	.3380	37.994
60	92.89	517.93	2.70	.0265	.3697	37.736
65	103.33	514.73	2.48	.0266	.4039	37.481
70	114.49	511.52	2.27	.0268	.4401	37.230
75	126.52	508.29	2.09	.0270	.4791	36.995
80	139.40	505.05	1.92	.0272	.5205	36.751
85	153.18	501.81	1.77	.0273	.5649	36.509
90	167.92	498.55	1.64	.0275	.6120	35.258
95	183.65	495.29	1.51	.0277	.6622	36.023
100	200.42	492.01	1.39	.0279	.7153	35.778
105	218.28	488.72	1.29	.0281	.7757	..
110	237.27	485.42	1.20	.0283	.8312	..
115	258.70	482.41	1.12	.0285	.8912	..

medium, but on the other hand it is impossible to liquefy the gas at temperatures above 31°C . or 88°F ., which is the critical temperature, and may frequently be exceeded in the condenser coils when the machine is used in hot climates. Failure to liquefy, however, does not entail a cessation of refrigerating action: what happens is that compressed gas is delivered into the evaporator coils instead of liquid, and by expanding into the cylinder causes a lowering of temperature. As the design of the machine is not suited to a cooling action of this character, the efficiency is slightly lowered when the condenser temperature exceeds 88°F . A further drawback to the use of carbon-dioxide is the extremely high working pressure, which at 50°F . is $46\frac{1}{2}$ atmospheres or 680 lb. per square inch (absolute) and 1080 lb. per square inch at 86°F . This high pressure necessitates stronger working parts than are necessary for an ammonia machine, and makes the prevention of leakage a difficult matter. At the same time, the existence of the higher pressure enables the desired cooling effect to be obtained with a smaller compressor, and consequently, for a given power, a carbon dioxide machine is less in size than an ammonia machine. Further, if any gas escaping from the machine should come into contact with stored food-stuffs, no taint is produced by carbon dioxide, whereas both ammonia and sulphur dioxide impart a most objectionable flavour to meat, etc. Taking all the factors into consideration, the choice between ammonia and carbon dioxide becomes difficult; the modern tendency, however, is to prefer the latter, except for the largest installations, influenced largely, no doubt, by considerations of space and the non-poisonous and inert character of carbon-dioxide. A table of constants of carbon dioxide is given on p. 289.

A comparison of the table on p. 289 with that given for ammonia shows that whilst liquid CO_2 has a much lower latent heat of vaporisation, a far greater weight of refrigerant is present in a given volume, which more than outweighs the inferiority in latent heat. For a given effect an ammonia compressor must possess seven times the volume required for a carbon-dioxide machine.

Sulphur-dioxide (SO_2) is also a cheap gas, and was first used by Pictet, of Geneva, in refrigerating machines. It is capable of easy liquefaction, has a fairly high latent heat of vaporisation, and does not attack metals if free from moisture. It is very poisonous, however, and owing to the low pressure at which it liquefies a relatively large compressor is necessary. One advantage of liquid sulphur-dioxide is that it acts as a lubricant to the moving parts, consequently no oil is necessary and the need for a separator obviated. In modern practice the use of sulphur-dioxide is restricted to minor refrigerating

CONSTANTS OF CARBON DIOXIDE (CO₂).*

Boiling Temperature Degrees F.	Gauge Pressure Atmospheres. = 14.7 lb. per sq. inch	Total Heat reckoned from 32° F.	Latent Heat of Evaporation. B.Th.U. per lb.	Increase of Volume during Evaporation	Weight of 1 cubic foot of Vapour lb.
-22	13.28	98.35	136.15	.4138	2.321
-13	15.27	99.14	131.65	.3459	2.759
-4	18.86	99.88	126.79	.2901	3.265
+5	22.26	100.58	121.50	.2438	3.853
14	25.93	101.21	115.70	.2042	4.535
23	30.08	101.81	109.37	.1711	5.331
32	34.76	102.35	102.35	.1426	6.265
41	39.74	102.84	94.52	.1177	7.374
50	45.25	103.34	85.64	.0960	8.708
59	51.24	103.59	75.37	.0763	10.356
68	57.75	103.84	62.98	.0577	12.480
77	64.85	103.95	46.89	.0391	15.475
86	72.47	103.72	19.28	.0147	21.519

* According to some makers of refrigerating machinery, this table stands in need of revision, as the figures in some cases do not agree with those obtained in practice.

operations, such as the cooling of dairy produce, or small-size cold stores. A sulphur-dioxide machine intended for working on the large scale would require a far larger compressor than an ammonia machine, and consequently considerations of space and material lead to the selection of other media. The chief constants of sulphur dioxide will be found in the following table:—

CONSTANTS OF SULPHUR DIOXIDE (SO₂).

Temperature, Degrees F.	Absolute Pressure in lb. per sq. inch	Latent Heat of Vaporisation, B.Th.U. per lb.	Volume of 1 lb. of Vapour in Cubic Feet
-4	9.27	171.0	8.06
+14	14.75	168.2	5.27
32	22.53	164.2	3.59
50	33.26	158.9	2.44
68	47.61	152.5	1.71
86	66.36	144.8	1.22
104	90.30	135.9	0.88

It will be observed that the pressure required to liquefy the gas at a given temperature is much less than in the case of ammonia; at 50° F., for example, the values are 33·26 and 88·96 lb. per square inch (absolute) respectively. This means that a less weight of the sulphur-dioxide is contained in a given space, and consequently that a larger compressor is necessary for a given cooling effect.

Other Media.—Apart from the three substances named, ether is the only other medium at present employed to any extent, and this only in cases where it is difficult to obtain fresh supplies of liquefied gases. Ether boils at 35° C., and may therefore be kept in ordinary bottles at most atmospheric temperatures.

Use of Brine in Cooling.—Two methods are available for removing the heat from a cold store or other place when the compression system is used. One is to allow the liquefied gas to evaporate in coils of piping distributed through the space to be cooled, and the other to circulate brine from a tank surrounding the evaporator coils through a system of pipes suitably placed in the cold store. The latter system is generally preferred, and possesses the advantage of acting as a storage of "cold"; as when once the pipes are filled with cold brine the machine may be stopped without risk of an undue rise in temperature, even for several hours. Brine is selected as the cheapest liquid that will not freeze at the temperatures employed. For moderately low temperatures a brine made by dissolving common salt in water may be used; for lower temperatures calcium chloride, which, being more soluble, forms a solution of lower freezing-point, is substituted for common salt. The properties of solutions of these salts are appended in tabular form (see p. 291).

The freezing-point of a saturated solution of calcium chloride is -40° C. (-40° F.), and of common salt -23° C. (-9·4° F.).

Types of Compression Machines.—Compression machines are made in a great variety of patterns, being procurable either combined with a steam engine or motor for driving purposes, or made so as to be belt-driven. Three types are selected for illustration, of which Fig. 79 represents a carbon-dioxide machine, horizontal land type, manufactured by Messrs. J. E. Hall, Ltd., of Dartford. The driving power is furnished by a compound steam engine, the cylinders being arranged tandem; the compressor being driven by a tail rod. The condenser and evaporator are separate from the machine, and may be fixed in any adjacent spot. Machines of this type are made capable of producing from 8 to 45 tons of ice in 24 hours, according to size.

Fig. 80 shows a steam-driven ammonia machine, of the vertical

PROPERTIES OF SOLUTION OF CHLORIDE OF CALCIUM (CaCl_2).

Degrees on various Scales			Specific Gravity at 60° F., Water = 1	Percentage of CaCl_2 by Weight	Weight of 1 Gallon of Solution			Freezing Temperature	
Salometer	Beaumé	Twaddell			Water	CaCl_2	Total	Fahr.	Centigrade
24	6	9	1.043	5	lb. 9.908	lb. 0.521	lb. 10.43	27.5°	- 2.5°
47	12	17	1.087	10	9.783	1.087	10.87	22.0	- 5.6
68	17	27	1.134	15	9.639	1.701	11.34	15.0	- 9.6
92	23	36	1.182	20	9.456	2.364	11.82	5.0	- 14.8
112	28	46	1.234	25	9.255	3.085	12.34	- 8.0	- 22.1

PROPERTIES OF SOLUTION OF CHLORIDE OF SODIUM (COMMON SALT).

Degrees on various Scales			Specific Gravity at 60° F., Water = 1	Percentage of Salt by Weight	Weight of 1 Gallon of Solution			Freezing Temperature	
Salometer	Beaumé	Twaddell			Water	Salt	Total	Fahr.	Centigrade
20	5	7	1.037	5	lb. 9.851	lb. 0.518	lb. 10.37	25.2°	- 3.8°
40	10	15	1.073	10	9.657	1.073	10.73	18.7	- 7.4
60	15	23	1.115	15	9.475	1.672	11.15	12.2	- 11.0
80	19	30	1.150	20	9.200	2.300	11.50	6.1	- 14.4
100	24	38	1.191	25	8.923	2.977	11.91	0.5	- 17.8

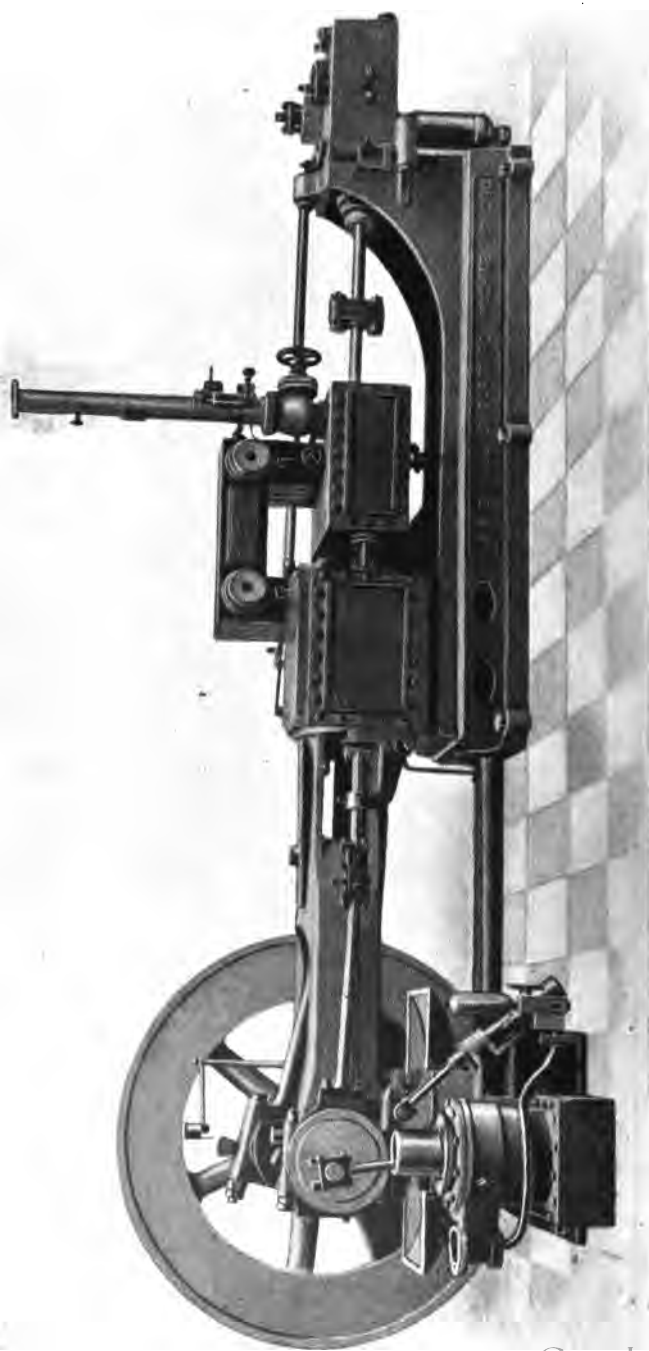


FIG. 79.—STEAM-DRIVEN CARBON-DIOXIDE MACHINE, HORIZONTAL TYPE.

type, made by the Haslam Foundry and Engineering Company, of Derby. The condenser coils are placed in the bed-plate, and a

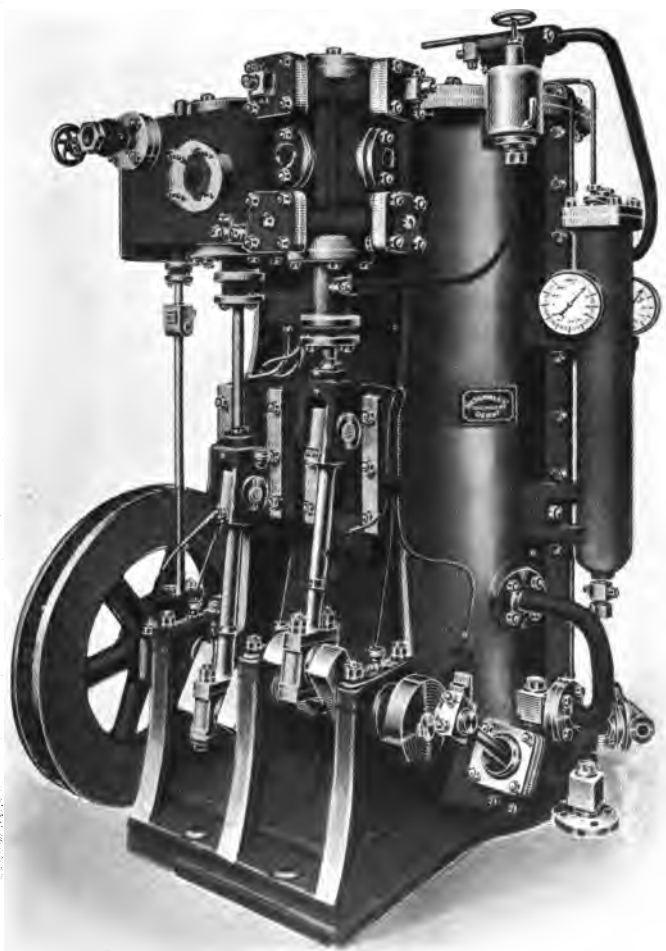


FIG. 80.—STEAM-DRIVEN AMMONIA MACHINE, VERTICAL TYPE.

water-pump is connected to the shaft for the purpose of circulating water round the condenser. A receiver for the liquefied ammonia is also provided. The steam engine and compressor are fixed side by

side, and the oil separator and gauges are placed at one side of the machine. This forms a convenient and compact machine for small cooling operations, particularly where space is a consideration.

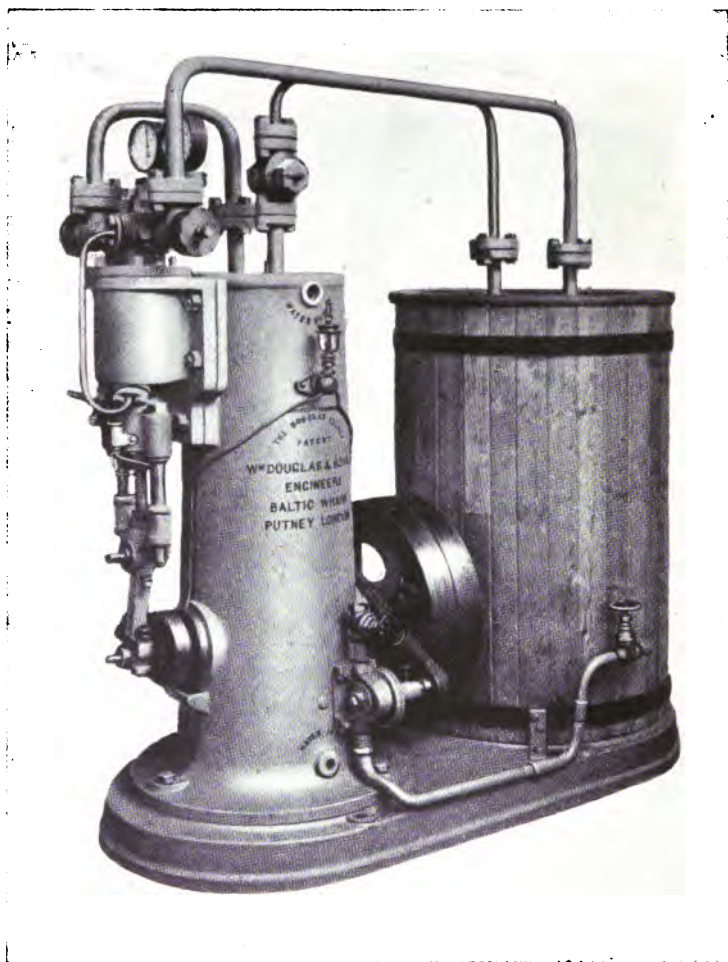


FIG. 81.—BELT-DRIVEN SULPHUR-DIOXIDE MACHINE.

The machine illustrated in Fig. 81 is a sulphur-dioxide refrigerator made by William Douglas and Sons, Ltd., of Putney, intended specially for dairies and small cold stores. It is driven by means of a belt, and by passing the shaft to which the compressor crank is

connected through the condenser tank, great steadiness is secured. The evaporator coils, surrounded by brine, are contained in a lagged tank on the base-plate, and pumps are provided for circulating the brine and cooling-water. The regulating valve is situated above the condenser tank. This machine is largely used in minor refrigerating operations; and may suitably be driven by a small suction-gas or other gas engine.

Description of Parts of Compression Machines. 1. The Compressor.

—The piston, and in larger machines the cylinder also, are best made from steel forgings, the piston being fitted with rings. The valves are made of tempered steel, and the seats of phosphor bronze or steel, bronze being inadmissible in ammonia machines. The piston rod moves in a gland filled with oil under pressure, which causes two cup-leathers to be squeezed against the piston rod, and thus prevents leakage. By maintaining the oil at a higher pressure than the enclosed gas—which is effected by a small pump—all possibility of leakage is prevented, and sufficient oil is taken by the rod into the cylinder to ensure proper lubrication of the piston. This oil is afterwards carried to the separator, and run out when necessary. Compressors are made either single or double-acting.

2. *The Condenser.*—Two types of condenser are used, viz., the submerged condenser, in which the coils are immersed in water in a tank through which a circulation is maintained; and the surface condenser, in which the pipes are exposed to the air, and water from a trough placed above allowed to trickle over. The submerged type is generally used for small machines, and in cases where the cost of water is not of moment; the surface type is more economical so far as cooling-water is concerned, as the latent heat of evaporation of the water is utilised in the cooling process. The tubes are made of wrought iron or mild steel, welded into continuous lengths. The condenser may be placed in any convenient position, and may be located at a considerable distance from the compressor.

3. *The Evaporator.*—This consists of coils of iron piping, which is surrounded by the medium to be cooled. In case of brine-cooling, the coils are placed in a tank through which the brine is circulated by a pump; when used without brine the coils are placed in the cold store, and the heat absorbed by the evaporating liquid extracted directly from the air.

4. *The Oil-Separator.*—In order to remove any oil carried over by the compressed gas in the form of spray, a chamber furnished with a baffle-plate is provided, situated between the compressor and condenser. The oil adheres to the baffle-plate, and gradually trickles

down to the bottom of the vessel, from which it may be withdrawn by opening a suitable cock.

5. *The Safety-Valve.*—The high pressures prevailing in compression machines render a safety-valve desirable, and these, when used, consist of a conical valve held on to its seat by a strong spring, which must be overcome before the valve lifts. Messrs. Hall, of Dartford, interpose a copper disc between the interior of the machine and the valve, which would burst under an undue rise of pressure, and allow the valve to come into action. Any loss of gas in ordinary working, due to a leaky valve, is thus avoided.

6. *The Expansion Valve.*—The essential feature of this valve is that the size of the opening between the condenser and evaporator must be capable of a very fine adjustment, as the quantity of liquid passing through determines the amount of evaporation which ensues in the coils, and hence the extent of the cooling. Numerous forms are made, some of which are elaborate in structure. A simple and effective valve is made by constructing a conical opening between the two sets of coils, which may be closed, either wholly or partially, by means of a conical plug, the extension of which is screwed and passes through a nut to the handle. Every gradation from fully open to completely closed is thus made possible.

Advantages of Compression Machines.—Compared with air-expansion machines, the greater efficiency, smaller size, and easier regulation of compressing machines confer upon the latter a great superiority. Not only can a far larger refrigerating effect be obtained for the expenditure of a given amount of energy, but the space occupied—a great consideration in many cases—and the prime cost of the smaller machine are much less than when the air-expansion system is employed. By the use of circulating brine the temperature of a cold store may be adjusted with greater precision than is attained by the ingress of cold air. In consequence of the advantages enumerated, compression machines are rapidly superseding those of the air-expansion type, both for use on land and sea.

The Absorption System.—Ferdinand Carré, of Paris, was the first to invent a machine working on the absorption system. It consisted of a boiler, containing a saturated solution of ammonia in water, and connected by a pipe to a chamber surrounding a vessel in which water was placed to be frozen. On heating the solution in the boiler, large quantities of the gas are expelled, and sufficient pressure is thereby generated to cause the gas to liquefy in the chamber, which, during this part of the operation, is placed in a tank of water to assist the condensation. The boiler is now removed from the fire or source of heat; and on cooling the solution re-absorbs the

ammonia gas above it, causing a partial vacuum in the chamber surrounding the water. Rapid evaporation of the liquefied ammonia ensues in consequence, and by extracting the latent heat of evaporation from its surroundings, causes the water to freeze. The solution in the boiler is now strong, and the operations may be repeated indefinitely.

The step from the intermittent action of F. Carré's machine to a continuous action was made soon after by many inventors, and in Britain Messrs. Pontifex and Wood took up the manufacture of absorption machines with considerable success, introducing many improvements which led to a widespread adoption in breweries and elsewhere. No other gas than ammonia has been used, as the combined properties of extreme solubility in cold water and almost complete expulsion on boiling, and the absence of corrosive action on iron, are not possessed

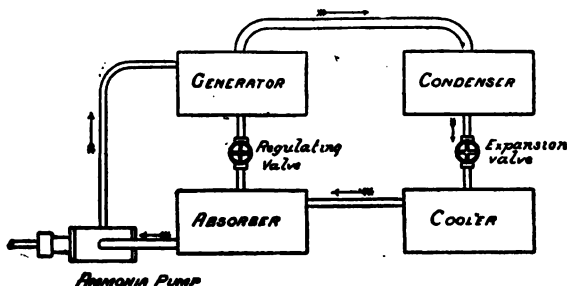


FIG. 82.—PRINCIPLE OF ABSORPTION REFRIGERATING MACHINE.

by other gases. At 16°C ., or 61°F ., water will absorb 760 times its volume of ammonia gas, which is almost entirely expelled on boiling. The points in favour of and against ammonia as a medium, already enumerated in connection with compression machines, apply to absorption machines also.

Principle of Modern Absorption Machines.—Modern machines working on the absorption system take many forms, but the general principle may be understood from Fig. 82, which represents the method adopted in the machines manufactured by Messrs. Ransomes and Rapier, Ltd., of Ipswich. A strong solution of ammonia in water is heated by steam-pipes passing through the generator, the gas being thereby expelled and driven over into the condenser. The large mass of gas driven off generates a pressure of 120 lb. in the condenser, which consists of a series of pipes surrounded by cold water. The gas liquefies under this pressure, and passes in the liquid state through an expansion valve of the same type as those employed in compression machines, into the cooler or evaporator, which also resembles the

corresponding part of a compression machine. From the cooler the gas passes into the absorber, which contains a cold, weak solution of ammonia, in which the gas re-dissolves, strengthening the solution, which is then pumped back again into the generator. The solution in the generator, as fast as it is deprived of gas by the heat of the steam coils, is allowed to trickle through a regulating valve into the absorber, through a cooling arrangement not indicated in the diagram, and, after absorbing a fresh quantity of gas, returns to the generator. The whole arrangement is such as to secure a continuous disengagement of ammonia gas, and consequently a continuous refrigerating effect. In order to prevent moisture being carried over by the ammonia gas, a water-separator or purifier is inserted between the generator and condenser.

It will be observed that the absorption system differs from the compression process only in the method employed to secure a continuous supply of liquefied gas, heat compression taking the place of mechanical compression. The appearance of the actual machine is depicted in Fig. 83, the various parts being constructed in the form of wrought iron cylinders which contain the coils of piping common to the generator, evaporator, condenser, and weak ammonia cooler; the whole being mounted so as to give compactness and easy access to the regulators.

Advantages and Drawbacks of Absorption Machines.—The chief points in favour of the absorption system are the almost entire absence of moving mechanism, and the ease with which the machine may be operated, even by unskilled labour. The upkeep of the plant is consequently less costly than in the case of compression or air-expansion machines, as there are fewer repairs and less labour required. Against this must be recorded the drawback of the necessity of a steam boiler as adjunct, whereas machines of the other types can be worked by motors, or a small oil or gas engine, in cases where steam is not available. The efficiency is about equal to that of the compression machine. On the whole, the absorption machine is well adapted for cooling operations in dairies, etc., where a skilled attendant is not at hand; and in making clear ice an economy can be effected by using the steam condensed in the process as the supply of distilled water for conversion into ice.

"Capacity" of Refrigerating Machines.—The capacity of a refrigerating machine may be expressed by the number of heat units extracted per hour from the evaporator* (or the ice-making equivalent of the heat

* The extraction of 12,000 B.Th.U. per hour from water at 0° C. or 32° F. is frequently taken as a unit of capacity, and is called "1 ton." It is equivalent to the production of 2000 lb. of ice in 24 hours from water at the freezing point.

extracted); or by the actual quantity of ice manufactured in a given time. In each case the temperature of the cooling-water and atmosphere must be specified. It is customary to take each of these temperatures as 55° F., and the time in the case of ice-making capacity

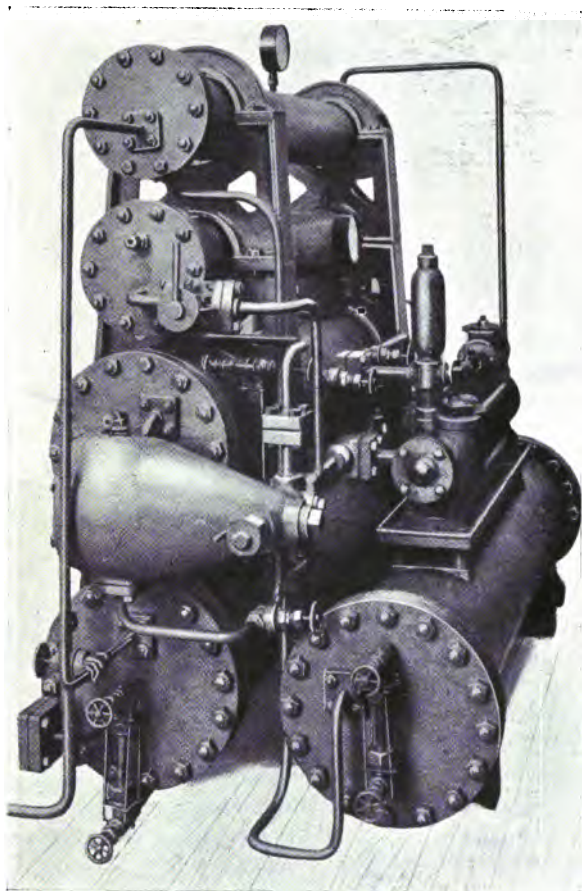


FIG. 83.—ABSORPTION MACHINE.

as 24 hours. Thus a machine capable of making 10 tons of ice in 24 hours is said to have an "actual" capacity of 10 tons. Owing to considerable losses in the ice-making plant itself, the capacity as measured by the heat extracted from the surroundings of the evaporator coils, will exceed the "actual" capacity. The former, which is

designated the "refrigerating" capacity, depends, as shown below, on the working temperature, but in ordinary working is usually about twice as large as the "actual" capacity.

"Energy-Ratio" of Refrigerating Machines.—In a heat-engine work is given out by taking in heat at a high temperature and rejecting heat at a lower temperature, the difference between the entering and leaving quantities being the equivalent of the work done by the engine. The "efficiency," or proportion of heat converted into work, is therefore expressed by the ratio

$$\frac{\text{Heat entering} - \text{heat rejected}}{\text{Heat entering}}$$

In a refrigerating machine matters are reversed ; the heat enters at the lower temperature (from the evaporator coils) and is rejected at a higher temperature (in the condenser). To make this possible, work must be furnished from an external source ; and the ratio of the cooling effect to the work expended in driving evidently decides the capability of the machine. This ratio is given by the expression

$$\frac{\text{Heat extracted}}{\text{Heat expelled} - \text{heat extracted}}$$

or

$$\frac{\text{Heat extracted}}{\text{Heat equivalent of work furnished}}$$

the work entering the machine being converted into heat, and being equivalent to the net amount of heat rejected. Various terms such as "coefficient of duty," etc., have been proposed for this ratio, which appears, however, to be best expressed by the designation "*energy ratio*," as suggested by the author. It will be shown later (Chapter XX.) that the quantities of heat expelled and taken in by an ordinary heat engine, or an inverse heat engine (refrigerating machine) are proportional to the absolute temperatures at which the heat leaves and enters. Applying this to a refrigerating machine, Energy ratio =

$$\frac{\text{Absolute temp. at which heat is extracted } (T_2)}{\text{Absolute temp. at which expelled} - \text{absolute temp. at which extracted} \over (T_1) \quad (T_2)}$$

or, expressed in symbols,

$$\text{Energy ratio} = \frac{T_2}{T_1 - T_2}$$

It is evident that the practical energy ratio will be less than the calculated, owing to the losses by friction, etc.; and the ingress of external heat. A fuller discussion of these points will be entered into in connection with the subject of thermodynamics; a few examples, however, will now be given to illustrate the use of the formula obtained.

Example 1.—The temperature of the cooling water supplied to the condenser of a refrigerating machine (and assumed to be equal to that of the contained medium) is 20°C ., whilst that in the interior of the evaporator is -60°C . To find the energy ratio.

Converting into absolute degrees, $T_2 = 213$, and $T_1 = 293$;

$$\text{hence energy ratio} = \frac{213}{293 - 213} = 2.66.$$

This means that the heat extracted from the surroundings of the evaporator coils would be 2.66 times as great as the heat equivalent of the work done in driving the machine, neglecting losses.

Example 2.—To compare the economy of an air-expansion machine which delivers 1 lb. of air at -40°C . with that of another machine which delivers 2 lb. at -20°C . into a similar store. Condenser temperature in each case = 25°C .

The amount of cooling due to the entry of 1 lb. of air at -40°C . is the same as that caused by 2 lb. at -20° . The energy ratio, however, differs in the two cases, being $\frac{233}{298 - 233} = 3.59$ and

$$\frac{253}{298 - 253} = 5.63 \text{ respectively.}$$

Hence for a given cooling effect, the machine working at the higher temperature would require less driving-power, in the ratio $\frac{3.59}{5.63} = \frac{1}{1.57}$; or, 1 H.P. in the second case would be equal in cooling effect to 1.57 in the first.

Example 3.—A carbon dioxide machine works at gauge-pressures of 18.86 ats. and 51.24 ats. in evaporator and condenser respectively. 10 H.P. are required to drive the machine, and the losses from various causes are 50 per cent. To find the capacity of the machine, i.e. number of tons of ice made in 24 hours from water at 15°C .

Reference to the table of constants of carbon dioxide shows that the temperatures corresponding to 18.86 and 51.24 ats. are -4°F . and 59°F ., or -20°C . and $+15^{\circ}\text{C}$. Hence the energy ratio, or

$$\frac{\text{heat extracted}}{\text{heat equiv. of work provided}} \text{ is equal to } \frac{253}{288 - 253} = 7.23.$$

Allowing for 50 per cent. losses, the figure becomes $\frac{7.23}{2} = 3.62$ (approx.). This means that every horse-power expended on the machine will extract heat equivalent to 3.62 H.P. from the water to be frozen. Hence 10 H.P. in 24 hours will extract

$$\frac{10 \times 33000 \times 60 \times 24 \times 3.62}{1400} = 1,229,000 \text{ lb.}^\circ\text{C. units (approx.)}$$

since 1400 ft.-lb. = 1 lb.-°C. unit. To convert 1 lb. of water at 15° C. into ice requires 95 lb.-°C. units; hence weight of ice made = $\frac{1229000}{95 \times 2240} = 5.78$ tons.

The examples given are intended to illustrate the general principles governing the working of the machines, and are not to be taken as applying to actual working conditions, which are influenced by many factors—such as atmospheric temperature, temperature of cooling water, internal friction of machine, etc. It is evident that economic working is secured by (a) keeping the condenser as cool as possible, and (b) working at as high a temperature as possible in the evaporator, consistent with obtaining the desired cooling effect.

If in the formula $\frac{T_2}{T_1 - T_2}$, T_1 and T_2 be equal, the energy ratio = infinity. The meaning of this is that when the condenser and evaporator are at the same temperature, no work is being done; and it will also be seen that the nearer T_1 and T_2 approximate, the greater will be the energy ratio—and consequently the economy of working—of the machine. If the evaporator temperature = 0° (absolute) in the formula, then the energy ratio = 0; which means that no amount of work can extract heat from a body at absolute zero. Other things being equal, the less the value of T_2 the less will be the energy ratio; that is, it becomes increasingly more difficult to extract heat from a substance as its temperature falls. The bearing of these points on the practical working of a machine of any type is obvious.

Working Data.—The results obtained in practice with a standard type of compression machine are given in tabular form on p. 303.

Taking the figures for the last machine in the list on p. 303, it will be observed that for an expenditure of 8 H.P. for 24 hours, 40 cwt. of ice are actually obtained. The work represented by 8 H.P. for 24 hours is

$$8 \times 33000 \times 60 \times 24 \text{ ft.-lb.}$$

CARBON-DIOXIDE MACHINES (H. J. West and Co., Southwark).

Brake Horse-Power Required	Ice-Making Capacity in 24 Hours	Heat Extracted in B.Th.U. per Hour, from Brine at			Capacity of Cold Store Reduced to 35° F. in Cubic Feet	Condensing Water at 55° F., Gallons per Hour
		25° F.	35° F.	45° F.		
1½	cwt. 3	4,000	5,000	7,000	300	48
2½	6	8,000	10,000	14,000	600	90
3	12	15,000	21,000	27,000	1300	150
4	20	25,000	35,000	45,000	2500	250
6	30	38,000	52,000	68,000	4000	320
8	40	50,000	70,000	90,000	5000	400

and the work equivalent of the heat required to freeze 1 lb. of water, originally at 56° F., is

$$778 \times 168 \text{ ft.-lb.}$$

since 24 B.Th.U. are required to cool the water to 32° F., and 144 B.Th.U. to freeze it. If the heat extracted were equal to the work done, the ice made in 24 hours would be

$$\frac{8 \times 33000 \times 60 \times 24}{778 \times 168} = 2927 \text{ lb.}$$

Actually, however, 40 cwt. or 4480 lb. are made, hence every H.P. of work done in driving the machine extracts from the ice plant heat equivalent to

$$\frac{4480}{2927} = 1.53 \text{ H.P.}$$

The heat extracted from brine at 25° F. is 50,000 B.Th.U. per hour, or 50,000 × 24 B.Th.U. in 24 hours. If no losses occurred in the ice-making plant, the weight produced would be

$$\frac{50000 \times 24}{168} = \frac{50000}{7} = 7143 \text{ lb. in 24 hours}$$

from water at 56° F. The radiation and other losses in the process are, therefore, equivalent to (7143 - 4480) × 168 = 447,500 B.Th.U. approximately, or nearly 37.5 per cent. of the total heat extracted.

Ice Manufacture.—Artificial ice is made by conducting cold brine from a refrigerating machine to a receptacle in which vessels con-

taining the water to be frozen are placed. After circulating round the vessels, the brine returns to the refrigerator, where it is again cooled and circulated. A small pump attached to the machine is employed to force the brine round the circuit. Occasionally the medium used in the machine is allowed to evaporate (or expand) round the ice-vessels, in which case brine circulation is dispensed with. Three chief systems are in vogue for producing artificial ice, known as the can, cell, and plate systems, and differing from one another in the details of procedure. A brief description of each system will now be given.

The Can System.—In this method the water to be frozen is placed in a galvanized iron vessel, rectangular in section, and tapering from the top downwards to facilitate the removal of the ice. A number of these cans are placed in a wooden trough, through which cold brine is circulated at a temperature of about 18°F. or -8°C. Ice forms first on the sides of the cans, and spreads gradually towards the centre, until the whole is frozen. The cans are then removed and inverted, and a jet of warm water made to play over the outside, which melts the layer of ice in contact with the can and so loosens the block, over which the can will now slide. This process is cheap and comparatively rapid, but the quality of the ice made is not of the highest.

The Cell System.—This differs from the foregoing in the respect that the water-vessels are fixed, and furnished with hollow walls between which the cold brine or medium circulates. These cells are generally cubical in shape, and consequently the block of ice produced will take longer to melt than that obtained from a can, as a cube possesses less surface in proportion to its mass than the truncated prism obtained in the can system. In order to remove the blocks of ice from the cells, a piece of rope is inserted in the top of the cell, round which the water freezes. Warm brine is then circulated round the cells to loosen the ice, which may then be hauled out by means of the piece of rope. Cell ice takes longer to form than can ice, but, generally speaking, is more compact.

The Plate System.—The mode of procedure adopted in this system is to freeze from one side only, to which end a hollow plate, through which brine or the medium may be circulated, is placed in a large tank containing the water to be frozen. Ice forms on the plate, and spreads outwards, being removed when the block has attained the desired thickness. This process is very slow, but the ice produced is of superior quality, being compact and durable. A number of such plates may be placed in the tank, and the ice removed

before the blocks spreading out from the opposite faces of adjacent plates are allowed to meet. Slow freezing always produces the most compact ice.

Different Kinds of Artificial Ice.—When ordinary drinking water, containing salts of calcium, etc., and dissolved gases, is frozen, an opaque ice results, which is soft and lacks durability, especially when quickly formed, as in the can system. The opaque character of the ice is mainly due to the liberation of the dissolved gases at the moment freezing occurs, the gas bubbles becoming entangled amongst the ice. The salts in solution are only set free to a slight extent in the layer of ice which first forms; thus in a can or cell the layers next to the walls are practically free from these salts. The chief separation of mineral matter occurs when the centre or core freezes, and hence this portion is generally more opaque than the rest of the block. In the plate system this drawback does not exist, as only a portion of the water in the tank is frozen, and the residue, rich in salts, may be removed and replaced by other water.

A much superior class of ice, both with regard to appearance and durability, can be secured by continuously agitating the water during the freezing process. The dissolved gases then escape, and a much clearer and more compact ice is obtained. Various kinds of mechanical agitators have been devised for this purpose; and the difficulty of the opaque core due to the salts present may be overcome by siphoning out the water in the centre, and replacing it by distilled water, when a block clear throughout can be obtained from either cans or cells.

The best form of ice, however, from every standpoint, is that made from freshly-distilled water. The waste steam from a steam plant may be utilised as the source of supply; and if recently condensed, it will be free from dissolved gases, and produce ice of great transparency and solidity. Care must be taken, however, not to use steam which is contaminated with the vapour of oil, derived from the engine in which it has been used.

The chief uses to which opaque ice is applied are the making of freezing-mixtures, the preservation of fish on fishing-boats, and the cooling of the small rooms used by butchers, etc., to store perishable articles of food in hot weather. For table use, or for addition to liquids for consumption, clear ice is employed. Such ice should be made from water of the highest degree of organic purity, and should be carefully protected from contamination during the manufacture. Many tradesmen still prefer natural ice (obtained chiefly from Norway) to refrigerator ice, claiming that the latter discolours and

imparts a taint to foods with which it is brought into contact. Such a result would be due to the use of impure water, or to carelessness during manufacture or subsequent storage.

Working Data for Can Ice.—The following data have been arrived at by Messrs. H. J. West and Co., for the ice-making plant manufactured by them :—

Weight of Ice Block	Size of Can	Time of Freezing in Temperate Climate	Number of Cans Required per Ton of Daily Output
lb.	in.	hours	
56	$4\frac{1}{2} \times 13 \times 33$	12	20
84	$6 \times 15 \times 33$	22	24
112	$8 \times 16 \times 33$	36	30
224	$10 \times 24 \times 36$	60	25
336	$12 \times 26 \times 36$	72	20

A rough guide as to the number of hours required to freeze a given block of ice of thickness S , in temperate climates, can be obtained by the use of the formula

$$\text{Time in hours} = \frac{7 S^2}{32 - t} + 1$$

where t is the temperature of the brine in degrees Fahrenheit, and S the thickness in inches of ice made in cans of dimensions similar to those given in the preceding table. Applying values in the formula, a block 6 inches thick would require 15 hours to freeze with brine at 14°F. ; and 19 hours with brine at 18°F. The formula assumes favourable working conditions all round, and gives a value less than that usually realised. Plate ice takes four times as long to make.

Cost of Ice-Making.—Taking into account labour, fuel, depreciation of machinery, lubricants, cost of water, etc., the cost of making ice should not exceed 3s. per ton. The larger the plant, the cheaper will be the ice, as the large machine is not only relatively more efficient than the smaller one, but requires practically the same amount of labour. Machines of actual ice-making capacity of 200 tons per 24 hours have been constructed, the cost per ton in such cases being considerably below the figure named.

Cold Storage.—As the successful preservation of food-stuffs and other perishable articles depends upon the maintenance of a low temperature, which must not be subject to wide fluctuations, it follows

that suitable arrangements for cooling continuously the room in which the articles are stored must be made. When the initial cooling has been effected, it is then only necessary to remove the heat which inevitably leaks in from the surrounding atmosphere through the walls of the store. It will be observed from the following table that the temperature to be attained is seldom more than a few degrees below freezing-point.

SUITABLE TEMPERATURES FOR STORING VARIOUS ARTICLES.

Name	Temperature in °F.	Temperature in °C.
Beef and mutton (fresh)	33 to 40	1 to 5
„ „ (frozen)	16 „ 25	-9 „ -4
Veal	35	1·5
Pork	35	1·5
Poultry and game	30 to 35	-1 to 1·5
Fish (fresh)	25 „ 32	-4 „ 0
„ (frozen)	16 „ 25	-9 „ -4
Milk	35	1·5
Cream	35	1·5
Butter	25 to 30	-4 to -1
Eggs	33 „ 35	0·5 „ 1·5
Cheese	32 „ 33	0 „ 0·5
Fruits	32 „ 40	0 „ 5
Beer (in barrel)	33 „ 40	0·5 „ 5
„ (bottled).	45	7·5
Vegetables	35	1·5
Furs	30 to 40	-1 to 5

The necessary reduction of temperature is achieved by one of the three following methods :—

1. Circulation of cold brine from the refrigerator through a system of pipes, or through hollow walls, or a combination of both.
2. Circulation of cold air by means of fans, or, in the case of air-expansion machines, delivering the cold air direct from the machine.
3. Circulation of the medium (ammonia, carbon-dioxide, or sulphur-dioxide) through pipes in the cold store.

Each of these methods will be considered in turn.

Cooling by Brine Circulation.—This method is most commonly

employed in cold stores, as it is not only capable of nice regulation, but enables the low temperature to be maintained for long periods, after the initial cooling of the articles, without working the machine. The large mass of brine in the pipes, with its high specific heat (0.9 or more), suffices to absorb all heat entering the store for long periods, before its temperature rises to a sufficient extent to endanger the articles stored. A much greater cumulative effect is thus obtained with brine than by either of the alternative methods of cooling.

The pipes containing the brine are located on the ceiling of the store, and consequently the air in contact with them becomes cooled and sinks downwards amongst the articles, warmer air from below rising to replace that which has fallen. This in turn is cooled by contact with the pipes, and thus a circulation of cold air is established. The cold pipes also absorb the heat radiated from the various objects, and finally the temperature of the store is reduced to the desired degree. Iron pipes are generally employed, and are not corroded to any great extent by solutions of common salt or calcium chloride, provided air be expelled. It is not advisable to galvanize the pipes, as corrosion then occurs to a marked extent.

In some cases the walls of the cold store are made hollow, and brine circulated through the space. This procedure greatly facilitates the cooling or freezing of articles hung on or near the walls, and also provides a large reserve of "cold" to maintain the low temperature when the machine is resting.

When the articles are to be frozen, and not merely chilled, a brine of low freezing point is requisite, and for this reason a solution of calcium chloride is preferable to one of common salt, which might freeze and choke the pipes. When a less intense degree of cooling is desired, a solution of common salt may be safely employed. The circulation of brine is maintained by means of a small pump coupled with the machine.

Fig. 84 illustrates the application of the brine system of cooling as applied in a vessel conveying a cargo of frozen meat. The brine is passed through a continuous length of piping, bent into parallel branches, and fastened to the ceiling of the cold chambers.

Cooling by Cold Air Circulation.—This system was originally employed in air-expansion machines, the cold air from the expander being delivered through suitable trunks into the cold chambers. Now that this type of machine has been almost entirely superseded by compression machines, cold air circulation, when adopted, is carried out by forcing air, cooled by contact with cold brine, into the chamber by means of fans. The procedure adopted at some of the London

docks is to allow the entering air to pass through a cascade of cold brine, falling over corrugated plates to give a large surface for cooling the air. Control of the temperature of the store is secured by regulating the quantity of cold air admitted, and the temperature of the brine from the refrigerator. The advantage secured by the method is the absence of fog in the store, as the entering air is deprived of its surplus moisture by the cold brine, and contains only the amount of moisture necessary to cause saturation at the entering temperature. A further advantage is that a better circulation of air amongst the

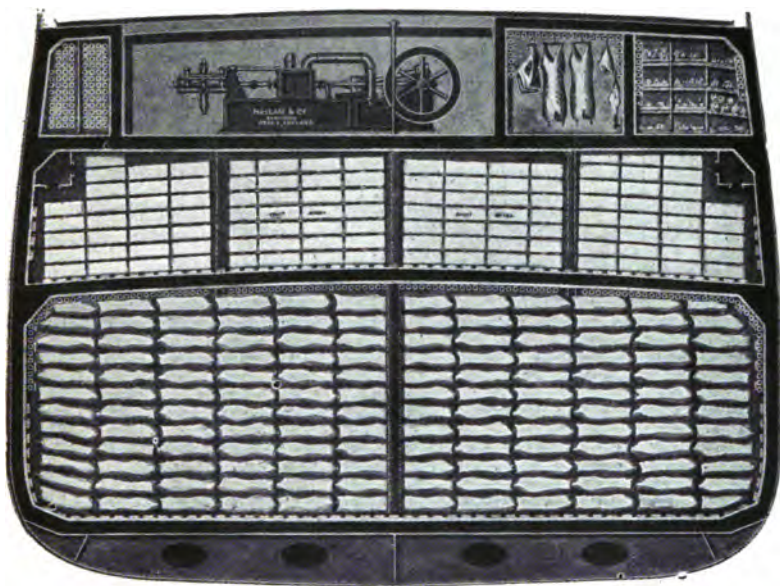


FIG. 84.—BRINE COOLING AS APPLIED TO A VESSEL.

articles stored is secured than in the case of cooling by brine pipes, as the existence of stagnant layers is not possible. On the contrary, the reserve of cold material is smaller, and consequently the periods during which the machine may be rested shorter, than when brine circulation is used; and the stored articles tend to become dry.

Cooling by Circulation of the Medium.—In this method the evaporator coils are continued into the cold store, and the liquid produced by the compression allowed to evaporate throughout the whole length, and thus cool the chamber. This procedure enables the use of brine to be dispensed with, and is in this respect more economical. A

drawback to its use is the leakage which almost invariably occurs, resulting, in the cases of ammonia and sulphur dioxide, in the tainting of stored food-stuffs. In addition, the control of temperature cannot be secured with the same degree of precision as in the case of brine or air circulation, and the reserve of cold material is small. This method is not employed to any great extent at the present time.

Insulation of Cold Stores.—As the maintenance of a low temperature in a cold store depends upon the removal of heat which enters through the walls from external surroundings, it is necessary to line the walls with materials which do not permit of the free transmission of heat. Any materials used, however, should not be liable to become damp by absorbing atmospheric moisture, as a large proportion of the cooling effect is then wasted in freezing this moisture. The insulating material, moreover, should not tend to become mouldy, as contamination of stored food-stuffs might result. The materials chiefly employed are cork, sawdust, charcoal, hair-felt, peat, and slag-wool, all of which are poor conductors of heat, and so largely prevent the ingress of heat from surroundings. The methods of applying these materials will be given in detail in the succeeding chapter.

Other Applications of Refrigerating Machinery.—Amongst the other uses to which refrigerating machinery has been applied, of which space does not permit of a detailed description, may be mentioned the cooling of milk and other dairy produce; the cooling of water in breweries; the cooling of chocolate; the freezing of the walls of borings in the earth to prevent ingress of water; the cooling of buildings in hot weather; and the production of ice for indoor skating-rinks. In the case of milk, cooling to below 10°C . immediately it is taken from the cow arrests the growth of germs almost entirely, and renders the milk much safer as an article of food. The cooling is effected by allowing the milk to trickle over the exterior of a corrugated drum, in the interior of which cold brine is circulated. The cooling of water and wort in breweries is usually effected by allowing the liquid to fall over a series of pipes containing cold brine.

CHAPTER XVII.

THE TRANSFER OF HEAT. CONDUCTION.

Methods by which heat may pass from one place to another.—If a piece of hot iron be placed on a slab of metal, its temperature will fall until it attains that of its surroundings. One portion of the heat lost has passed into the slab on which it rests by the process known as “conduction”; a second portion has been removed by the air in contact with the iron becoming hot and rising, colder air taking the place of that which has risen, and in turn removing another portion of the heat, the circulation thus set up being termed “convection”; whilst another part of the heat has escaped in the form of energy waves from the surface, to which method of heat transfer the term “radiation” is applied. If the hot iron were suspended in air by a non-conducting thread, the heat would escape entirely by convection and radiation; whilst if similarly suspended in a vacuum, the cooling would be due entirely to radiation. The first of these three methods, viz. conduction, forms the subject of the present chapter.

Conduction.—When one end of a bar of metal is placed in a fire, a rise in temperature may be observed in the portions outside the fire. The molecules of the metal in the fire, as the temperature rises, are set into a more rapid state of vibration, and communicate this enhanced movement to adjacent molecules, which, in turn, affect the molecules in their own vicinity, and thus an increased rate of movement is conveyed to the molecules in the remote portions of the bar. This increased speed is identical with a rise in temperature, and consequently the process of conduction is in reality a mechanical transfer of heat energy.

Good and Bad Conductors.—Conduction takes place with greater facility in metals than in any other substances. For this reason a piece of metal feels colder to the touch than wood or felt, although the actual temperature is the same in each case; the reason being that the metal conducts away the heat of the hand more rapidly, and thus gives rise to the sensation of cold. Non-metallic solids, liquids and gases are, in general, feeble conductors of heat.

Coefficient of Conductivity.—The rate at which the temperature rises in a given part of a substance, remote from the heated part, depends not only on the freedom with which heat energy is conducted but also on the specific heat of the material. Thus 1 calorie imparted to 1 gram of lead would cause a rise in temperature of about 32°C. , whilst if imparted to 1 gram of aluminium the rise would be only 4.5°C. Hence it cannot be inferred that, if two bars of metal be placed with one end exposed to the same source of heat, the bar which most quickly attains a given temperature at a point away from the source of heat is the better conductor. If judged in this manner, as Tyndall showed, bismuth would appear to be a superior conductor to iron, whereas the actual *quantity* of heat passing along the bismuth is much less than in the case of iron. The coefficient of conductivity, which refers to the quantity of heat energy passing through a substance, is defined as follows:—

The *coefficient of conductivity* is the number of heat units transmitted in one second from one face of a cube of unit side to the opposite face, when the difference of temperature between the opposite faces is 1 degree.

The units may be chosen in any given system. It is evident that in any actual case of conduction, the heat passing will vary directly as the time and area of section, and it is customary to assume that the heat passing varies directly as the difference of temperature between opposite ends, and inversely as the thickness, which is practically correct within certain limits. The heat units passing are evidently directly proportional to the coefficient of conductivity of the material. Expressing this in algebraic form:

Heat units transmitted =

$$\frac{K \times \text{area of section} \times \text{time in secs.} \times \text{diff. of temp. between faces}}{\text{thickness or distance between faces}}$$

where K = coefficient of conductivity. Examples illustrating the use of this equation will be given later.

Determination of Coefficients of Conductivity.—Several methods have been employed to determine the coefficients of conductivity of various substances. The method adopted by Forbes for metals is shown in Fig. 85, and consisted in maintaining one end of the bar at a constant high temperature, and noting the steady reading of a series of thermometers inserted in holes drilled in the bar, in which mercury was placed to secure a metallic contact with the thermometer bulbs. A considerable time is required to attain a steady condition, but this

is finally reached when the heat passing along the bar in a given time is exactly equal to that lost by radiation and convection from its surface. If the quantity conducted should exceed that which escapes, the temperature will rise, and conversely, if the heat lost were greater than that arriving from the source, the temperature would fall. Evidently, therefore, the two quantities are equal when steady readings are furnished by the thermometers.

A second experiment with the bar was then performed, indicated to the right of the figure. The bar was heated to the same tempera-

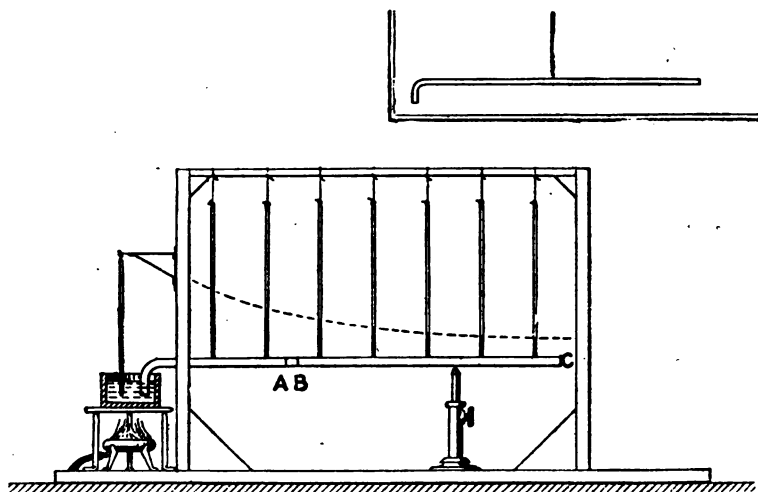


FIG. 85.—FORBES' CONDUCTIVITY EXPERIMENT.

ture throughout in a bath, and cooling readings taken at definite intervals of time over a range compassed by the highest and lowest temperatures indicated by the thermometers in the previous experiment. As the bar was at the same temperature throughout, one thermometer in the centre sufficed for the readings. The object of the second experiment was to determine the actual quantity of heat lost by the bar per second at any given temperature, and, from the data furnished by the two experiments, the coefficient of conductivity was calculated.

The exact calculation is somewhat complicated, but the principles involved may be understood by reference to the following example. Imagine a portion of the bar, *AB*, 1 centimetre long. The difference in temperature between *A* and *B* can be obtained by drawing pro-

jectors on to the curve formed by joining the readings of the thermometers, and the area of section may be obtained by measurement. All the heat passing from A to B goes on to the rest of the bar and is lost by radiation and convection from the portion BC when the steady state has been reached. It remains to be found how many heat units per second escape from the part BC under the existing conditions, and this figure is obtained from the second experiment. If the whole bar weigh W grams, and has a specific heat S , and if it be observed that C calories per second are radiated at the average temperature existing between B and C in the first experiment, the heat escaping from the whole bar would be $(W \times S \times C)$ calories per minute, and from the portion BC the number escaping would be $\left(\frac{W \times S \times C \times \text{length of BC}}{\text{total length of bar}} \right)$ calories per second. This is equal to the number of calories passing from A to B in the steady state, and as all the above values are known, the coefficient may be obtained from the equation :—

Calories passing from A to B =

$$\frac{K \times \text{area of section} \times 1 \text{ second} \times \text{diff. of temp. between A and B}}{\text{distance between A and B}}$$

all of the quantities being known except K , the coefficient, which in this case would be expressed in C.G.S. units.

This method cannot well be employed in the case of badly-conducting materials, as a thermometer placed a few inches from the hot end would scarcely be affected by the small amount of heat reaching it. The successful carrying out of the experiment involves the provision of a steady temperature at the hot end, a constant atmospheric temperature, and prolonged observation to ensure that the steady condition has actually been reached.

Amongst other methods which have been used for determining the coefficient of conductivity of solids, mention may be made of the following: A plate of the solid is placed between the ends of two thin copper cylinders, so as to make a good contact with each. Steam is passed through one cylinder, whilst the other is filled with ice. After a given time the water resulting from the melting of the ice is tapped off and weighed, and by multiplying the weight of ice melted in grams by 80, the number of calories passing in the given time is determined. The area, thickness, and difference of temperature between the faces being known, the value of K may be obtained as in the previous equation. This method may be applied to bad

conductors as well as metals ; but many precautions are necessary to ensure concordant results.

The coefficient of conductivity of liquids has been determined by placing the liquid under experiment in a thin, wooden cylinder, and floating a quantity of hot liquid on the cold. Horizontal thermometers were placed at different levels, and from the readings of a consecutive pair the difference between the upper and lower levels of a given stratum were known. The heat passing through this stratum in a given time was determined by multiplying the weight of the liquid below the stratum by its specific heat and average rise in temperature, the remaining data being the thickness of the stratum and the area of section of the cylinder. The calculation is the same as in the previous cases. A small quantity of heat is conducted along the wooden cylinder, but in most cases this is small in comparison with that transmitted down the column of liquid.

No satisfactory method has yet been devised for determining the conductivity of gases, as it is practically impossible to obtain two perfectly steady layers at different temperatures, owing to convection and diffusion.

Numerical Values of Coefficients of Conductivity.—The following table gives the numerical values of the coefficients of conductivity of a number of substances, the figures chosen being the average of several determinations made by different methods. In some instances considerable differences exist between the figures obtained by different observers for the same substance. The heat unit employed is the calorie, the area of section 1 square centimetre, distance between faces 1 centimetre, time 1 second.

It is only in very special cases that the figures (page 316) can be applied to calculate the quantity of heat transmitted through a material under working conditions. In the first place, the value of the coefficient varies greatly with the temperature. With metals, the conductivity decreases with the temperature ; the figure for iron, for example, diminishing from $\cdot 16$ at 0°C. to $\cdot 13$ at 100°C. , and $\cdot 11$ at 300°C. With badly conducting materials, or insulators, the conductivity increases with the temperature in some cases, but diminishes in others. A further drawback, from the standpoint of practical utility, is that the figures hold true for an arbitrary condition seldom realised in practice—that of two surfaces kept at a uniform temperature and shielded from radiation losses and air convection. As an example, the coefficient for air under these ideal conditions is given as $\cdot 000051$; but if an air-space be employed over a hot surface to prevent escape of heat, the effective value, owing to con-

COEFFICIENTS OF CONDUCTIVITY.

Substance	Range of Temperature	Coefficient of Conductivity, C.G.S. units
<i>Metals—</i>	°C.	
Silver	7 to 15	1·096
Copper	"	1·00
Aluminium	"	0·345
Zinc	"	0·295
Brass	"	0·265
Iron	"	0·160
Tin	"	0·153
Lead	"	0·084
<i>Non-Metallic Solids—</i>		
Sandstone	0	0·0107
Ice	"	0·0023
Glass (crown)	7 to 15	0·0021
" (Jena), various	"	0·0011 to 0·0020
Sand	"	0·00074
Oak, across fibres	"	0·00059
Fir, along fibres	"	0·00047
" across fibres	"	0·00026
Cork	"	0·00040
Pine sawdust	"	0·00024
" shavings	"	0·00016
Dry asbestos	"	0·00030
Silicate cotton (slag-wool)	"	0·00015
Wool	"	0·00012
Hair-felt, sheets	"	0·00011
<i>Liquids—</i>		
Water	10 to 20	0·00140
Glycerine	"	0·00064
Alcohol (ethyl)	"	0·00055
Ether	"	0·00034
Benzene	"	0·00033
Paraffin oil	"	0·00045
Turpentine	"	0·00031
<i>Gases—</i>		
Hydrogen	7 to 10	0·00033
Marsh gas	"	0·000065
Carbon monoxide	"	0·000050
Air	"	0·000051
Carbon dioxide	"	0·000027

vection, is 0·0002, or 4 times as great. Any figure for practical use must be obtained from tests carried out under working conditions, and it frequently arises that a material inferior for a given purpose from the standpoint of absolute conductivity, proves superior in practice, owing to the difference between working and ideal con-

ditions. Examples of such practical tests are given later in the chapter.

It is interesting to note, in the case of metals, that the numerical order for heat conductivity is the same as that for electrical conductivity. The figures for consecutive metals, however, do not bear the same ratio to one another in the two cases. Water is the best liquid conductor (except mercury); and taking the figures for gases as reliable, it would appear that the conductivities are in the inverse order of the densities, that is, the lighter the gas the better it will conduct heat.

A few examples will now be given to illustrate the use of the coefficients in calculating the heat transmitted through materials.

Example 1.—The walls of a cold store are 20 cm. thick, and have a total area of 100 square metres. If the external temperature be 25° C., the internal temperature -5° C., and the coefficient of conductivity of the material of the wall .0003, find the number of heat units which must be removed in 1 hour to prevent a rise in temperature. From equation on page 312,

$$\begin{aligned} \text{Calories passing through} &= \frac{.0003 \times 3600 \times 1000000 \times 30}{20} \\ &= 1,620,000 \text{ calories; the time being reduced to seconds and the} \\ &\text{area of surface to square centimetres. Dividing by 252, the answer} \\ \text{in B.Th.U. is } &\frac{1620000}{252} = 6430. \end{aligned}$$

This result would assist in deciding the size of the refrigerating machine required.

Example 2.—To compare the quantities of heat transmitted through a copper plate 1 inch thick, and an iron plate of the same area, but $\frac{1}{2}$ inch thick. For equal thicknesses, under the same temperature conditions, the quantities would be directly as the conductivities viz. 1 to .16. As the iron plate is only one-half as thick, the ratio will be 1 to .32, or about 3 to 1 in favour of the copper.

Uses of Good Conductors of Heat.—The good conductivity of copper renders it the most serviceable metal to employ for the fire-boxes of locomotives, where it is necessary rapidly to generate a large quantity of steam. Although the copper firebox is thicker, to ensure mechanical strength, than would be necessary if steel were used, the vastly superior conducting power of copper enables a much greater quantity of steam to be raised in a given time. In stationary boilers, where space is not so great a consideration, an increased heating surface enables iron to take the place of copper, thus effecting a great

saving in the prime cost. The actual surface temperature of the metal in the firebox or flue is much less than that of the flames, owing to the rapid conduction of the heat impinging upon it through the material to the water, and also to the existence of a layer of gas, cooled by contact with the plates, on the surface.

The good conductivity of copper explains the efficiency of this metal in the construction of soldering-"irons." When the tip of the soldering-iron or bit is laid on the work, the surface of the metal operated on abstracts heat from the bit, and lowers the temperature of the point. Heat flows rapidly from the main portion of the bit to the cooled tip, and thus maintains the temperature necessary to effect the operation.

The safety-lamp, invented by Sir Humphry Davy, is a further example of the utilisation of good conductors. If a piece of wire gauze be held over a gas-burner, and the gas be turned on, it may be ignited above the gauze and burn on the upper surface, without the flame striking through to the jet. The heat of combustion is rapidly conducted to the remote portions of the gauze, so that for a considerable time no part of the metal is raised to the temperature of ignition of the gas. Hence, if a lamp be surrounded by gauze, explosive gases in a mine may find a way through the meshes and burn in the interior of the lamp—thus warning the miner of the danger existing—but the gases cannot burn externally until the gauze is raised to the temperature of ignition.

Uses of Bad Conductors, or Heat Insulators.—The various kinds of clothing which serve to protect the body from cold, are examples of heat insulators. Obviously, the thicker the material the less will be the heat escaping from the surface of the body to the surrounding air. Woollen materials, furs and silks are superior in this respect to cotton fabrics. Other examples are found in the use of wooden handles for smiths' tools, which prevent the heat of the tool from reaching the hand; and the superiority of stone, brick or wooden houses over corrugated iron structures, which are notoriously hot in summer and cold in winter. One of the most useful applications of heat insulators, from an engineering standpoint, is the protection of boilers, steam-pipes, etc., from loss of heat to the atmosphere, and of cold stores from ingress of heat. This application will now be specially dealt with.

Heat Insulation.—If a boiler or steam-pipe be exposed to air, a serious loss of heat is occasioned, and a further drawback arises, in the case of a steam-pipe or the exposed cylinder of a steam-engine, owing to the condensation of the steam in considerable quantities.

This condensation, in a long bare steam-pipe, causes a considerable fall in pressure, and the accumulation of water in the cylinder of an engine is dangerous, as the end might be forced off. Again, a low temperature in a cold store would be very difficult to maintain unless the walls were properly insulated, and consequently a larger refrigerator would be necessary. In all such cases, it is customary to protect the surfaces with heat-insulating materials, which are commercially known as "*laggings*." Materials suitable for boilers and steam-pipes are not of necessity advantageous to employ for cold stores, and *vice versa*; and it will therefore be convenient to treat the two cases separately.

Heat-Insulating Materials for Hot Surfaces.—The properties desirable in a lagging for hot surfaces may be enumerated as follows:—

1. It should possess a low heat conductivity.
2. It should be non-inflammable, as it may frequently be exposed to sparks from furnaces.
3. It should not tend to crack when subjected to fluctuations of temperature, as otherwise it would in time become detached.
4. The mechanical strength should be sufficient to enable it to resist vibrations and accidental blows.
5. It should be capable of resisting the action of water or steam.
6. The specific gravity, especially when a thick coating is used, should not be so high as to place an undue weight on steam-pipes.
7. It should not cause corrosion of the lagged surface.
8. As a minor qualification, the specific heat should be as low as possible, as this means a less absorption of heat by the lagging when starting from the cold.

No single substance possesses all these features in a marked degree, and in choosing a lagging for a given purpose due regard should be paid to the properties which are of the greatest importance in the particular case. Many substances which are excellent non-conductors, cannot be used on account of failure to subscribe to the other conditions. A vacuum jacket should be an ideal lagging, but is not practicable.

Superiority of Porous Materials.—Experiment and practical use show conclusively that porous materials, or those which contain cavities enclosing air, are by far the most efficient non-conductors of heat. The pores should be sufficiently small to prevent convection currents in the enclosed air, but not so small as to cause too numerous lines of solid contact through the mass. The author has found, in the case of lagging made up in porous form, differences of 15 per

cent. in the conductivities of samples which were supposed to be identical, caused by variation in the size of the pores.

Tests for Thermal Efficiency of Laggings for Hot Surfaces.—The heat passing from a hot surface through a lagging is disposed of partly by radiation from the exterior, and partly by convection currents set up in the air in the vicinity. As the radiating powers of the surfaces of different laggings vary considerably, tests for absolute conductivity only, in which the surface is shielded from radiation, do not suffice to settle the question of practical efficiency. Moreover, it is frequently desirable to know the number of heat units escaping under working conditions, and in order to obtain this figure it is necessary to perform the test in a manner which realises these conditions. Two chief methods are employed for this purpose, which will be described separately.

Condensed Steam Test for Laggings.—A 4-inch or 6-inch steam-pipe is coated with the material to a definite thickness, and dry steam at constant pressure admitted. After the pipe has become thoroughly heated, the water condensed in the warming-up process is allowed to drain off, and the steam allowed to pass through the pipe for a definite time—say two hours. At the end of this time the water condensed is drained off and weighed, and represents the weight of steam which would condense under the given conditions. Knowing the latent heat of steam at the temperature employed, the number of heat units escaping may be calculated.

There are several objections to this process. Firstly, it is difficult to procure perfectly dry steam, and it is doubtful whether the water-separators fixed at the entrance and exit of the pipe secure complete dryness. Secondly, it is necessary that the steam should be kept at a steady pressure (and temperature) during the whole of the experiment, which involves a special boiler, an elaborate outfit and great care. Thirdly, as the result of a test of many hours' duration, only one result is obtained, viz., that for a given thickness at a given temperature. To obtain a variety of results for different thicknesses at different temperatures would extend the duration of the experiments over some months.

The table opposite, which represents the results of a test carried out by this method at the National Physical Laboratory, serves to show the nature of the observations and the manner of expressing the results.

The Electrical Heat Test for Laggings.—In this test the uncertainty arising from the use of steam of doubtful dryness is avoided by heating a steam-pipe internally by means of an electric current. In

RESULTS OF TESTS ON COVERING 1½ IN. THICK.

—	Lagged Pipe	Bare Pipe
Steam pressure (gauge)	219 lb. per sq. in.	ditto
Steam temperature	395° F.	395° F.
Temperature of air	70° F.	70° F.
Steam condensed per hour	5·22 lb.	23·65 lb.
Latent heat of steam at 395° F. in B.Th.U. } per lb.	838	838
Difference between steam and air tem- } peratures	325° F.	325° F.
Loss of heat per hour in B.Th.U. . . .	4375	19,820
Loss from bare flanges, ditto	2165	2,165
Net loss from pipe per hour, ditto	2210	17,655
Steam condensed by pipe only (effect of } flanges eliminated), lb. per hour	2·64	21·06
Area of pipe surface, sq. ft.	16·81	16·81
Steam condensed per sq. ft. per hour	0·157	1·25
B.Th.U. escaping per sq. ft. per hour	131	1048
ditto ditto ditto for } each degree F. excess temperature of steam over air	0·40	3·23

Percentage of saving effected by lagged pipe over bare pipe

$$= \left(\frac{1048 - 131 \times 100}{1048} \right) = 87\cdot7$$

a series of tests carried out by Professors S. P. Thompson and Dalby, a 6-inch steam-pipe, about 5 feet long, was covered to a known thickness with the material, and heated internally by passing a current through a length of "eureka" wire in the interior. An external resistance was placed in the circuit, and served to control the temperature of the pipe, which was read off from a series of thermometers which passed into the interior. An ammeter in the circuit, and a voltmeter across the terminals of the heater, served to indicate the rate at which energy entered, as 1 volt × 1 ampere = 0·24 calorie per second, or 0·057 B.Th.U. per minute. The external resistance was regulated until a steady internal temperature was attained, when the heat escaping through the covering would of necessity be equal to that entering. This quantity was found by multiplying the readings of the voltmeter and ammeter to obtain the

Y

watts entering the pipe, and $(\text{watts} \times 0.057) = \text{B.Th.U. escaping per minute}$. The results could then be expressed in the usual manner as B.Th.U. escaping per square foot of lagged surface per hour; and, by adjusting the resistance, the escape of heat at several different temperatures was obtained.

The electrical heat test, conducted in the manner described, is more reliable than the steam test, but still suffers from the disadvantage that a long time is required to obtain a steady temperature, owing to the large amount of material employed. In order to overcome this drawback, the author made a number of experiments

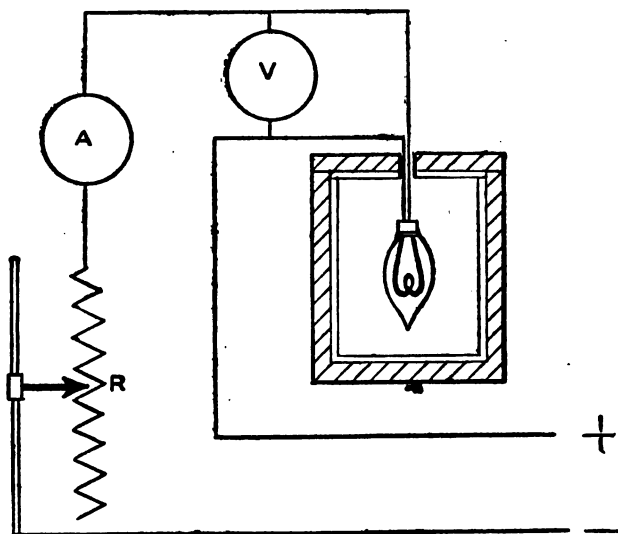


FIG. 86.—ELECTRICAL CONNECTIONS OF TEST FOR HEAT-INSULATING MATERIALS.

on a smaller scale, and found that it was possible to obtain results of equal accuracy in a much shorter time by the uses of the apparatus illustrated in Figs. 86 and 87. A piece of steam pipe, approximately 8 inches long and 6 inches diameter, and possessing 1.5 sq. ft. of external surface, is coated with the material under test. Passing into the interior is a 32-candle-power lamp, with carbon filament, which serves as the source of heat. The electrical connections are shown in Fig. 86, where A is the ammeter, V the voltmeter, and R the adjustable resistance. Fig. 87 is reproduced from a photograph of the apparatus, and shows the various parts. The voltmeter

should be capable of being read to 1 volt, and the ammeter to 0.1 ampere. A continuous wire resistance of 250 ohms enables a very fine adjustment to be obtained, and suffices for either a 100-110 or 200-220 volt circuit. Moving coil ammeters and voltmeters are best for direct current, and hot-wire instruments for an alternating current. The temperature is registered by means of a thermometer passing into the interior, the bulb of which is located about half-way down the cylinder, and mid-way between the lamp and inner wall. The bulb is shielded from the direct rays of the lamp by means of a piece of thin brass tubing, and under these



FIG. 87.—TEST FOR HEAT-INSULATING MATERIALS.

circumstances gives a true reading of the average internal temperature. If necessary, the cylinder may be made gas-tight, and the interior connected to a mercury column, when the exact internal temperature may be calculated from the increase of pressure, as in the constant volume air thermometer.* This refinement, however, is hardly necessary for commercial tests, and gives readings not differing greatly from those of a thermometer inserted in the manner described.

Before commencing readings, the lagging must be thoroughly dried, either by placing on the top of a furnace, or *in situ* round the test-pipe. The ammeter and voltmeter are then kept at a steady

* See description by the Author in "Engineering," Dec. 6, 1907.

reading by means of the resistance until the thermometer remains stationary for 15 minutes, when each is read. The current is then reduced by about .05 ampere, and a second stationary temperature obtained, and so on over the range of temperature desired. The product ($\text{watts} \times .057$), as before, gives the B.Th.U. escaping per minute, and as the external surface is 1.5 sq. ft., $\frac{2}{3}$ of the product gives the B.Th.U. escaping per sq. ft. per minute. The test may then be applied to other thicknesses of material, and complete data respecting the heat losses at all working temperatures obtained for all thicknesses in a far shorter time than is possible with large-scale tests.

Many interesting points concerning the thermal efficiency of laggings may be noted in the results obtained by the author during a long series of tests conducted by this method on different laggings. As an example, the data furnished by a covering material composed of 85 per cent. of light magnesium carbonate and 15 per cent. asbestos fibre, known as Newall's Magnesia Covering, are appended in graphic form. Fig. 88 is a curve obtained by plotting B.Th.U. lost per sq. ft. per hour against corresponding thickness of lagging, the internal temperature of the pipe being 400°F. , and the outside temperature 68°F. It will be seen that the saving effected by the first $\frac{1}{2}$ inch is 815 B.Th.U., by the second $\frac{1}{2}$ inch 900 B.Th.U., and by the succeeding $\frac{1}{2}$ inch layers 930, 950 and 960 B.Th.U. respectively. The curve is approximately hyperbolic, and an infinite thickness would be requisite to prevent any loss whatever. The noteworthy feature of the curve is the marked decrease in steepness beyond the ordinate representing $1\frac{1}{2}$ inches, indicating a rapidly diminishing saving power on the part of material added beyond this thickness. The curve corresponding to an internal temperature of 550°F. does not show such a marked falling-off until near the 2-inch ordinate; and hence the general practice of using a lagging $1\frac{1}{2}$ inch thick for temperatures up to 400°F. , and 2 inches for higher temperatures, has a sound scientific basis. For inferior materials, a greater thickness is necessary to secure an equivalent result.

The actual thickness to which a pipe should be lagged, in a given case, to secure maximum economy, can be obtained by considering the circumstances in conjunction with a curve of the type shown in Fig. 88. Experience must dictate the probable time that will elapse before the lagging must be renewed, and the price of fuel and number of working hours must also be taken into account. The number of B.Th.U. furnished by one pennyworth

of average coal, taking into account flue losses, etc., is, roughly, 100,000. Hence if the estimated life of the lagging in hours be multiplied by the B.Th.U. escaping per sq. ft. per hour, and the product be divided by 100,000, the answer will be the value in

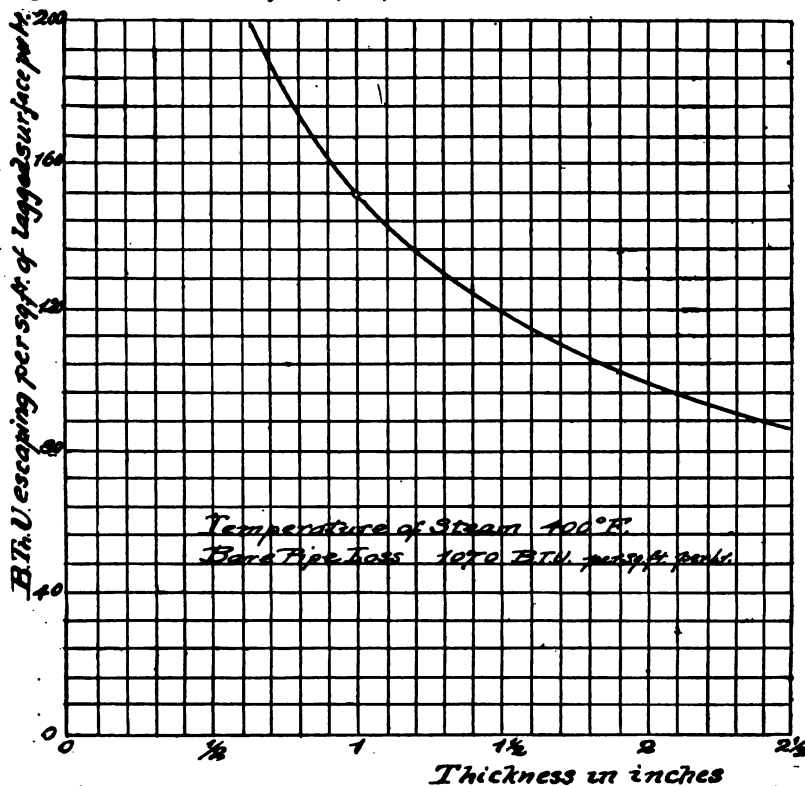


FIG. 88.—CURVE SHOWING HEAT ESCAPING FROM A PIPE CONVEYING STEAM AT 400° F., WHEN LAGGED WITH DIFFERENT THICKNESSES OF MAGNESIA.

pence of the escaping heat. If this calculation be performed for several thicknesses, it will be found that beyond a certain point a further thickness of lagging will cost more than the monetary equivalent of the additional heat saved. An example is appended, derived from the results obtained with the material under notice.

Example.—A pipe is to convey steam at 550° F. To find the most economic thickness to use of a lagging for which the following

data were obtained, the duration of the cover being estimated at 30,000 working hours:—

MONEY EQUIVALENT OF HEAT LOST IN 30,000 HOURS.

Bare pipe, per sq. ft.	490 pence
With $\frac{1}{2}$ -inch lagging	110 "
" 1 " "	70 "
" $1\frac{1}{2}$ " "	55 "
" 2 " "	46 "
" $2\frac{1}{2}$ " "	40 "
" 4 " "	33 "

From the above figures it will be seen that the saving effected by successive layers of $\frac{1}{2}$ inch over that of the underlying thickness is 380, 40, 15, 9, and 6 pence respectively, a further $1\frac{1}{2}$ inch only effecting an additional saving of 7*d.* per square foot of lagged surface in the time named. If $2\frac{1}{2}$ -inch covering were 6*d.* per foot dearer than 2-inch, the limit of economy would be $2\frac{1}{2}$ inches; if more than 6*d.* per foot dearer, a less thickness than $2\frac{1}{2}$ inches would be more economical for the estimated period. It should be remembered that each additional layer has a greater diameter, and therefore contains more material than the one beneath. The cost of material therefore increases progressively with the thickness; on the other hand, the labour charges for fixing are much the same, whatever the thickness.

The effect of temperature on the heat escaping through a lagging is indicated in Fig. 89, for different thicknesses, the temperature of the surrounding air being 68° F. The curves show a gradually diminishing steepness as the temperature rises, indicating an improvement in insulating power at higher temperatures. This improvement is often manifested by very porous materials, and may be due to the expulsion of excess of air as the temperature rises. As this expulsion is gradual, it is necessary, in making a test, to heat the material to a high temperature for some time before commencing readings.

It will be noticed that the curves diverge as the temperature rises, all having an origin at a point on the axis of temperature represented by 68° F. Hence the saving effected by the thicker coating becomes proportionately greater as the temperature rises. By taking the units represented by the distance between the two curves at any given temperature, and proceeding as in the foregoing example, the temperature limit above which the thicker lagging would be cheaper may be determined.

The temperature gradient through a magnesia lagging is depicted graphically in Fig. 90, and was obtained by inserting thermal junctions at different depths. The normal prolongation of the curve

would indicate a surface temperature of 96°F. , whereas the application of a junction to the surface showed 80°F. only. The former is probably correct, the latter being too low owing to radiation from the junction itself. For lower pipe temperatures a less steep gradient is obtained, the surface temperature being little altered. Too much reliance, therefore, cannot be placed on conclusions drawn from

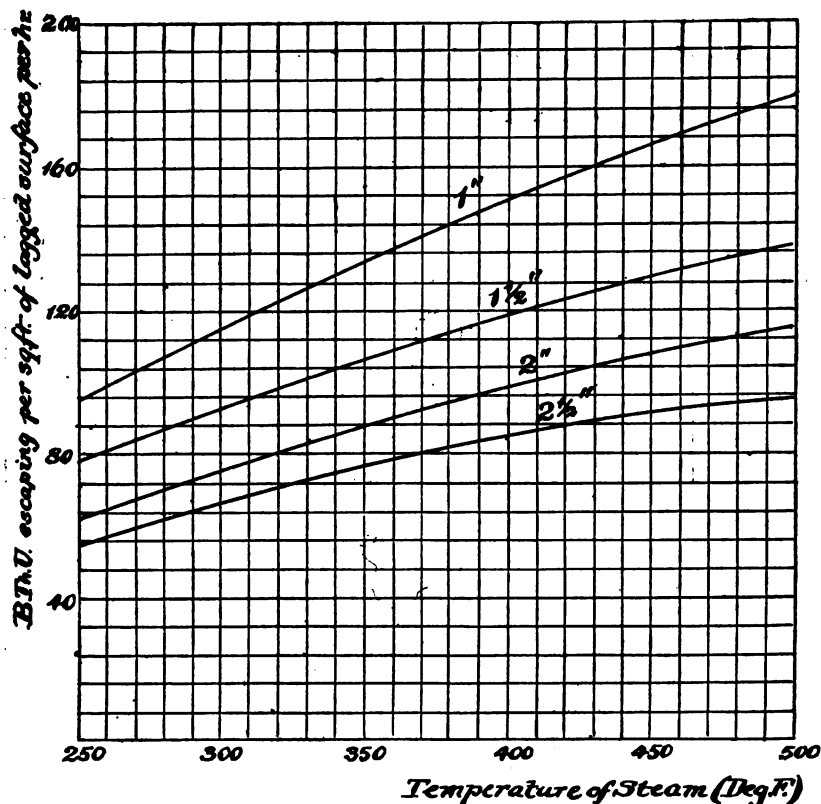


FIG. 89.—CURVES SHOWING LOSS OF HEAT THROUGH PIPES LAGGED WITH MAGNESIA AT DIFFERENT TEMPERATURES.

the observation of surface temperature, as the actual quantity of heat escaping is not indicated by this alone.

Effect of Surface on Insulating Power.—A rough surface radiates heat more freely than a smooth one, and all lagging should therefore be finished smooth. This is generally done by applying paint or varnish. Colour is of little moment, as for non-luminous radiations

all colours are practically identical in radiating power. A coating of metallic paint—such as aluminium—is best of all, owing to its smoothness, and reduces the heat escaping from an ordinary surface of lagging by about 7 per cent. This means that for every 100 B.Th.U. escaping from each square foot of lagged surface per hour in the

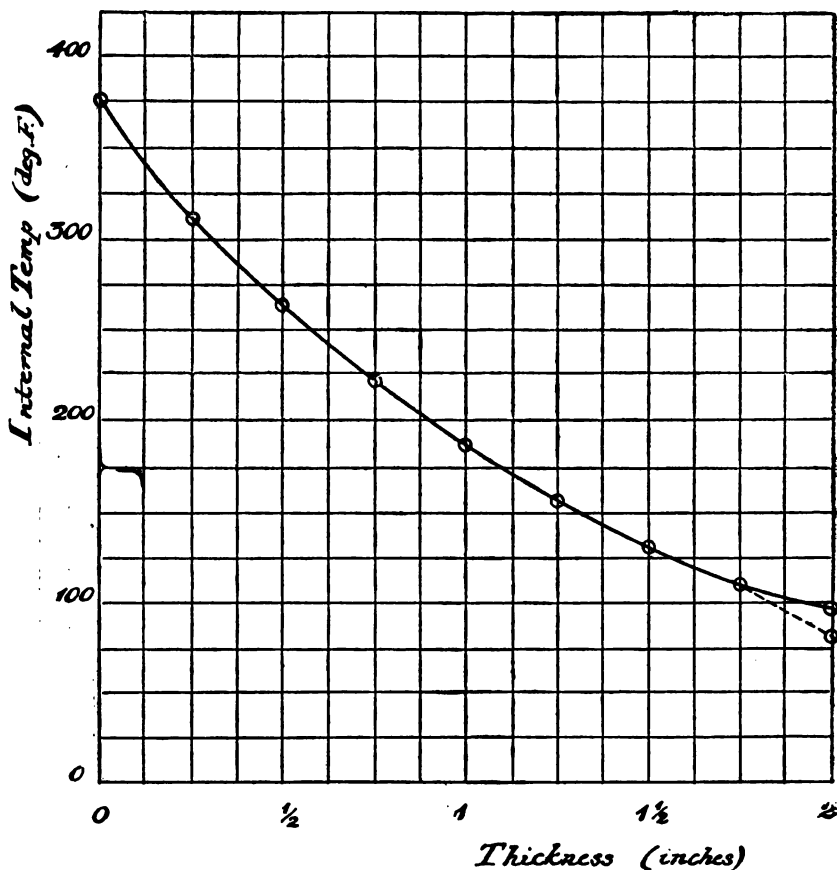


FIG. 90.—TEMPERATURE GRADIENT THROUGH MAGNESIA LAGGING.

ordinary way, only 93 would escape if a coating of aluminium paint were used. Whether the 7 units saved would ultimately repay the extra cost of the paint, depends upon the life of the lagging and cost of ordinary and metallic paint. A smooth surface, owing to its retention of heat, feels warmer to the touch than would a rough

surface under the same conditions of internal temperature. Hence the test often applied to form an idea of the efficiency of a lagging—that of feeling with the hand—may give an entirely erroneous indication unless the nature of the surface be taken into account.

Insulating Values of Materials in Common Use.—The following table shows the insulating value of a number of the best types of lagging at present in use. In modern engineering practice, such materials as dung, plaster-of-Paris, etc., are seldom used, the extra expenditure on a better lagging being justified by the diminished condensation of steam in the pipes, greater durability, and a lower atmospheric temperature in a closed engine-room. A good lagging is essential also in cases where it is desired to convey steam to a considerable distance without a notable fall in pressure. In locomotive work, also, the present tendency is to use a better-class insulator, such as magnesia, to cover the boiler, instead of the layer of felt and air-space formerly employed.

TABLE OF INSULATING VALUES OF LAGGINGS, EACH $1\frac{1}{2}$ INCHES THICK.

Name	B.Th.U. escaping per sq. ft. per Hour, at Steam Temperature of 400° F., External Temperature = 68° F.	B.Th.U. escaping per sq. ft. per Hour, for each Degree F. excess Temperature of Steam at 400° F. over External Air
Newall's Magnesia Covering	118	0.36
Blue asbestos	121	0.365
Mica (best form only)	123	0.37
White asbestos sectional covering, inferior types of mica and magnesia }	126	0.38
Plastics, best make (salamander composition, Kieselguhr, Leroy's plastics, etc.), and inferior asbestos sectional }	133	0.40
Plastics, cheaper and inferior varieties	143	0.43
Bare pipe	1070	3.23

Fall of Pressure along a Steam Pipe.—The temperature, and consequently the pressure, of steam in a pipe falls along its length, owing to the escape of heat from the surface. The extent of this fall may be calculated, for a given case, as indicated in the following example:—

Example.—Steam enters a 4-inch steam pipe at 400° F. = 245 lb.

(absolute) pressure per square inch. It is conveyed at the rate of 8000 lb. per hour; to find the temperature and pressure at the end of 100 feet—(a) when lagged so that the average loss of heat per sq. ft. per hour is 120 B.Th.U.; (b) when unlagged, with an average loss of 850 B.Th.U. per sq. ft. per hour.

The total surface of the pipe $= \pi dl = \frac{22}{7} \times \frac{1}{3} \times 100 = 105$ sq. ft. Hence the heat escaping in one hour from the lagged pipe $= (105 \times 120) = 12,600$ B.Th.U., and from the bare pipe $= (105 \times 850) = 89,250$ B.Th.U. The total heat of 1 lb. of steam at 400° F. (from tables) $= 1233$ B.Th.U., hence the total heat of 8000 lb. at 400° F. is 9,624,000. The total heat of the steam at the end of the pipe will be $(9,624,000 - \text{heat lost}) =$

9,611,400 B.Th.U. in the lagged pipe, and
9,534,750 „ in the bare pipe.

Dividing each of these numbers by 8000, to obtain the residual total heat per pound of steam, the figures are 1201·4 and 1191·8 respectively.

From tables, the temperature and pressure corresponding to a total heat of 1201·4 B.Th.U. per lb. are 393·8° F. and 230 lb. per sq. in. absolute pressure, which will be the values at the end of the lagged pipe; and similarly the figures for the bare pipe will be found to be 362° F. and 157 lb. absolute pressure.

Hence the fall in temperature in the lagged pipe is 6·2° F., and in pressure 20 lb. per sq. in.; whilst in the bare pipes the corresponding figures are 38° F., and 93 lb. per sq. in.

Descriptions of Laggings in Practical Use.—A material may be made up in the form of “sectional” covering, in which case it is shaped beforehand to fit the object to be lagged, and applied in sections bound together by strips of metal, the advantage gained being easy application and removal. For large surfaces such as the exterior of boilers, the “mattress” form is frequently adopted, the material being contained in loose form in a cover woven from asbestos or other material so as to secure pliability. The third form is known as “plastic,” the material being mixed with ingredients such as clay, etc., which impart adhesive properties, and applied to the surface with a trowel. In this case, the removal is difficult, and entails the destruction of the covering; hence this method is only adopted where the lagging is expected to be permanent. Many varieties of each type are sold, some of which, together with their chief features, are indicated below.

Newall's Magnesia Covering.—This consists of 85 per cent. of light magnesium carbonate, intimately mixed with 15 per cent. of asbestos fibre, pressed into the desired shape when moist. On drying, the mixture adheres sufficiently to permit of use without crumbling. As a heat insulator it is unsurpassed, being extremely porous; it will not stand rough usage, however, and does not resist the continued action of water or steam. It is very light, and does not exert any corrosive action on metallic surfaces. This material is largely employed in the British Navy, the lagging being protected by thin plates of planished iron from accidental damage. It may also be used in mattress form, and is made by the Magnesia Coverings Company.

Mica.—This lagging is composed of flakes of mica bound together by wire netting, or enclosed in covers to form a mattress; or better still, as made by the Mica Boiler Covering Company, the flakes may be cemented together by silicate of soda. The thermal efficiency of this material depends greatly on the quantity of air enclosed between the mica flakes, and in the best specimens is nearly equal to magnesia; but if carelessly made the covering is much less efficient. It is liable to peel if subjected to rough usage, but can be protected by thin sheet-iron. It is uninjured by water or steam, and the sectional material made by moulding the mica with silicate of soda, and afterwards baking, is particularly serviceable in damp places.

Asbestos Coverings.—Of the different varieties of asbestos, the white and blue are used for lagging purposes, either in sectional or mattress form. White asbestos laggings are much used, and although inferior to magnesia or mica as heat insulators, are less expensive. In the "Viceroy" covering, made by the United Asbestos Company, the efficiency is increased by building up the cover from corrugated strips, thus enclosing more air spaces. As asbestos is capable of being woven, it forms a suitable material for making insulating ropes, which may be wound round small steam-pipes used for temporary purposes, and many firms supply such ropes in different thicknesses. The fibres of blue asbestos are more tenacious than those of the white variety, and in the mattress coverings made by the Cape Asbestos Company the cover is woven of blue asbestos, and is filled with thin fibres of the same material. These coverings will stand a considerable amount of rough usage without injury, and may be saturated with water without deterioration; but are more expensive than the white asbestos laggings. Blue asbestos is also superior in insulating power to white.

Slag-Wool or Silicate Cotton.—This material is produced by

blowing steam through molten slag, and consists of fine fibres composed of silicates of lime and iron, resembling wool. It is enclosed in a suitable cover, and applied in mattress form to the hot surface. It is one of the best heat insulators known, but when subjected to vibration tends to crumble into powder, and thus to leave portions of the surface unprotected. It is also said to produce corrosion and pitting of iron surfaces, especially when moisture is present, and these two drawbacks have prevented its extensive use for hot surfaces. These objections do not apply to cold stores, for which it is largely used.

Plastics.—The expenses incidental to the manufacture of sectional or mattress coverings are obviated in this class of coverings, and cheaper materials may be used. A common substance used in the making of plastics is Kieselguhr or fossil meal, which is a highly porous form of silica of organic origin. This is made into cement by the admixture of sufficient binding material, and applied with a trowel, forming one of the best laggings of this type from the standpoint of thermal efficiency, but lacking in mechanical strength. Greater durability is secured—at the expense of insulating power—by the introduction of other materials; some of the compositions on the market containing asbestos, magnesia, mica, etc. Amongst plastics which enjoy a well-deserved reputation amongst engineers may be mentioned the “Kieselguhr” laggings made by Messrs. A. Haacke and Co., The “Salamander” covering made by the United Asbestos Company, the various compositions made by Messrs. F. Leroy and Co. and the “Eagle” cement of Dick’s Asbestos Company. Although inferior, as a class, in heat-insulating value to sectional coverings, plastics are cheaper and often mechanically stronger.

Choice of a Lagging.—In selecting a lagging for a given purpose several points must be considered. If liable to rough treatment, mechanical strength is of primary importance; whilst to convey steam long distances with a minimum fall of pressure, high insulating power is the first consideration. In a closed engine-room it is advisable to employ a lagging with a surface temperature as low as possible. Other points to be noted are liability or otherwise to dampness, and the probable time which will elapse before renewal becomes necessary. The last-named is of importance, as in a short period the superior efficiency of an expensive material does not cover its extra cost over a less efficient, but cheaper, covering. It is obviously impossible to prescribe a lagging which will be the most economical under all conditions, and the choice must be guided by existing circumstances. Having decided on a material, the correct

thickness to employ may be determined from the thermal constants of the substance, as indicated on page 326.

Heat-Insulating Materials for Cold Surfaces.—The fact that the temperature of a substance used to insulate a cold store never rises above that of the surrounding atmosphere—or water, in the case of a ship—enables many materials to be used which could not with safety be applied to hot surfaces. The essential features of a good material for lagging a cold surface are :—

1. Good insulating power.
2. No tendency to absorb atmospheric moisture.
3. Not liable to become mouldy, or to attract vermin.
4. Low specific gravity, particularly when used to insulate a ship.
5. Low cost.

The substances most used are silicate cotton, cork, charcoal, peat, sawdust and hair, the first-named being the most extensively used, as, in addition to its excellent insulating qualities, it is practically vermin-proof. Charcoal, owing to its lightness and cheapness, is much used to insulate the sides of the vessel from the chambers containing the frozen cargo. Powdered cork is good for the same purpose, but is more expensive. Peat and sawdust are frequently used on the score of cheapness, but are inferior in insulating power. Hair is a cheap and good insulator, but by no means vermin-proof, and lacks the cleanliness of other materials.

The most reliable tests of the insulating value of the substances enumerated have been made by lagging a box to a given thickness, and placing a block of ice in the interior, which has been carefully weighed before placing in the box. After the lapse of a definite time, the ice is taken out and re-weighed, and from the loss in weight the escaping heat may be calculated. An equal thickness of another material is then placed round the box, and a similar block of ice inserted. The substance which shows the least ingress of heat, as judged by the ice melted, is the best insulator. The results, however, may be varied to such a large extent by altering the density by close or tight packing, that it is difficult to state which is the best material. Beyond a marked inferiority in the cases of peat and sawdust, no statement as to the efficiency of the remainder may be made without prescribing the degree of compactness—preferably as so many pounds per cubic foot. Even if such data were available, however, no conclusions of great value could be drawn from them, as the material only forms a portion of the complete insulation, as will be seen later. A series of experiments performed with the completed

lagging would be necessary to furnish reliable data to guide in calculating the ingress of heat under given conditions. At present only a few such experiments have been recorded; but a fairly safe guide to the heat passing into the store may be obtained by assuming the coefficient of conductivity to be 0.00025 to 0.0003 calories per second per square centimetre of surface, for each centimetre of thickness of a well-made partition or wall.

Construction of Insulating Walls of a Cold Store.—In general, the insulating wall of a cold store is constructed of wood, so as to enclose air spaces, damp-proof courses, and spaces filled with insulating material. Of the large number of patterns existent, one will be selected to indicate the general principle of construction, and is shown in section in Fig. 91. The brick wall is coated with tar to render it damp-proof, and batons of wood, 2 inches by 4 inches in section, are nailed on at intervals. Over these is fastened a double

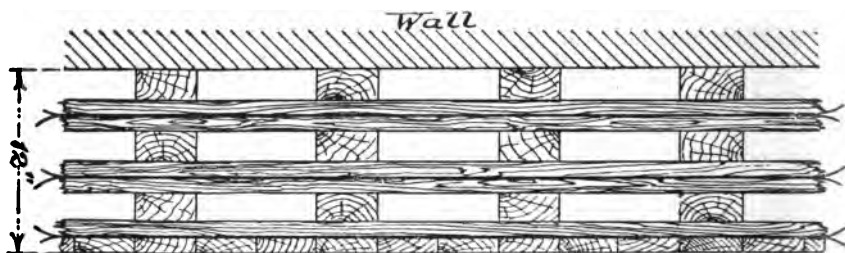


FIG. 91.—METHOD OF INSULATING A COLD STORE.

layer of matchboarding, 1 inch thick, a layer of impregnated paper being placed between the boards as a damp-proof course. Then follow a second set of batons, a second double layer of matchboarding—also with damp-proof paper between—a third set of batons, and finally a double layer of matchboarding, the inner layer laid horizontally and the outer layer vertically; the total thickness being 12 inches. The space nearest the walls is an air space, made so that any moisture penetrating the wall will have difficulty in passing through the structure. If this space were filled with insulating material the water would readily creep through to the layer of matchboarding. The two remaining spaces are filled with silicate cotton or other insulator. The prepared papers known as “Ruberoid” make an excellent damp-proof course between the boards. In American practice the filling of the air spaces with insulating material is not adopted to the same extent as in this country, ordinary air spaces only being frequently employed.

On vessels carrying a frozen cargo, the space between the outer shell and the store rooms is filled with charcoal or other insulating material, the heat of the sea-water and atmosphere thus being largely prevented from entering.

The domestic ice-safe consists of a metal chamber separated by an air-space from the wooden exterior. The saving effected by this air space, as common experience shows, is considerable.

Diffusivity.—This term was applied by Lord Kelvin to the quotient $\frac{\text{coefficient of conductivity}}{\text{specific heat of unit volume}}$. It expresses numerically the thickness of a plate of a substance which would be raised 1° by the heat conducted through a plate of unit thickness in 1 second, when the difference of temperature between opposite faces is 1° . For example, if a plate of aluminium 1 cm. thick, of area x square centimetres be kept with opposite faces 1° C. different, the calories transmitted in 1 second will be $(x \times K) = .345 x$, the coefficient of conductivity being .345. The specific heat of unit volume of aluminium—that is, the number of calories required to raise 1 cubic centimetre by 1° C.—is .61. Hence the number of cubic centimetres raised 1° by .345 x calories is $\frac{.345 x}{.61} = .565 x$. The thickness of a plate of area x square centimetres, and volume .565 x is .565 cm., and the same result will evidently be obtained whatever be the value of x . The diffusivity of aluminium, therefore, is expressed by the number .565. For other metals the diffusivities are as under:—

Copper	1.205
Silver	1.86
Zinc	0.435
Iron	0.184
Tin	0.374
Lead	0.24

The significance of these figures will be understood by considering the case of two bars of different metals, of equal section, placed with one end in a hot space, a thermometer being inserted in each case near the hot end. The increase of temperature indicated by the thermometers will be most rapid in the bar possessing the greater diffusivity, and hence bars of tin and lead would show a more rapid rise in temperature than iron, because the quantity conducted by these metals in one second—although less than that conducted by the iron—operates on materials of low specific heat, and thus produces a greater rise in temperature. As the bars become heated along

their length, however, the heat passing through is no longer expended in causing a rise in temperature, and proceeds onwards to the rest of the bar; hence, when the steady state is reached the highest temperatures are observed in the materials possessing the greatest conductivities.

The diffusivities of different kinds of rocks have been determined by Lord Kelvin and others, and the results applied in observations of the fluctuations of temperature in the earth's crust in different localities.

Heating of Masses of Metals in Furnaces.—The time required for the complete heating of a mass of metal when placed in a furnace evidently depends upon the diffusivity of the metal. In many instances, such as the annealing of large masses of steel, it is essential that the centre of the mass shall attain a sufficiently high temperature, if the operation is to be successful. At present, manufacturers are largely guided by experience as to the time a block of steel or other material is allowed to remain in the furnace, but reliable data on the point would be of the highest value. Such data could be obtained by noting the temperature indicated by a thermo-electric pyrometer inserted in blocks of different sizes, under given conditions of furnace temperature. The following results were obtained in this manner for steel billets of circular section, which were placed when cold in a furnace at 1300° F. The temperature of the furnace was then raised to 2000° F., and the time required for the centre of each billet to reach 1900° F. noted.

Diameter in Inches	Time in Hours	Diameter in Inches	Time in Hours
18	3½	32	10
20	4	40	15½
24	5½	41	16½
28	7½	42	17
30	8½	45	19½

From the above figures it will be seen that the time required varies directly as the area of section, and this would probably apply to all cases.

CHAPTER XVIII.

THE TRANSFER OF HEAT. CONVECTION.

Nature of Convection.—The molecules of a liquid are capable of moving amongst each other with a certain degree of freedom, whilst those of a gas are almost perfectly free to move. A disturbance of equilibrium in either liquids or gases is consequently followed by a movement tending to restore equilibrium, and when heat is the disturbing cause this movement constitutes what is termed convection.

If a vessel of water be heated from below, the lower portions, owing to expansion, become less dense than those above, and rise in consequence, being replaced by colder water from above. This continues until the temperature of the whole mass has been brought to the boiling point, and hence the transfer of heat from the source has been effected by convection. If the heat be applied at the upper surface, the less dense liquid remains floating on the top, and does not mix to any extent with the colder liquid below. Any heat communicated downwards will be due to conduction, and as liquids are bad conductors the process is extremely slow. Conversely, the temperature of a mass of liquid may be cooled throughout by reducing the temperature of the upper portion—as occurs in the freezing of a pond of water—whilst if the lower portion only be cooled the upper layers are practically unaffected. The same reasoning applies to gases, in which case, however, a mixing of hot and cold gas may occur to some extent in opposition to gravitation, owing to the property of diffusion. The phenomena connected with the transfer of heat by convection are of the greatest importance in many engineering problems, and will be studied in this connection in the present chapter.

Circulation of Water in Boilers.—The two objects to be secured in a boiler of any type are (1) to obtain as large a heating surface as possible, consistent with strength, and (2) to ensure that all the water in turn shall come into contact with the heated surface. The latter

condition involves placing the fire at the lowest practicable level, so that the effect of convection may be as great as possible.

In the locomotive boiler the firebox is separated from its casing at the sides by a space of about 2 inches, which space is occupied by water. The crown of the firebox is covered to a varying depth with water; and a series of brass tubes pass longitudinally from the firebox through the barrel to the smoke-box and chimney. Heated water is therefore arising by convection from the sides and crown of the firebox, and from the tubes. All the water above the tubes and top of the firebox is therefore set into circulation and heated just in the same manner as water is boiled on a fire, but the water in the lowest part of the barrel would remain practically stagnant were it not for the fact that a large portion of the firebox is at a lower level than the barrel; hence convection from the sides of the firebox establishes the necessary circulation in the water beneath the tubes, and circulation is secured in every part of the boiler. When once the water is boiling, the steam generated maintains an efficient circulation by rising to the top of the boiler from all the heated parts.

In stationary boilers of the horizontal type the flues are placed as low as possible in the casing, so that the bulk of the water is above the hot surface. By the use of cross-tubes in the flue, placed at various angles, the lowest portions of the water are enabled to circulate, and the additional advantages of increased heating-surface and strength are secured. In the vertical type the main mass of water is above the flue, and the fire at the bottom; hence the water in the space between the flue and casing can rise freely, being replaced by colder water from above. Cross-tubes are sometimes used to ensure greater strength and increased heating-surface.

In water-tube boilers the tubes are filled with water and heated externally, as distinct from the tubes in a locomotive boiler, which are heated internally and surrounded by water. The tubes containing the water pass from the furnace to the barrel containing the main supply, and from which the steam is drawn off, this barrel resting on the top of the furnace. The heated portions of the tubes are inclined, so that as the hot water rises by convection into the barrel a fresh supply of cold water passes in at the other end. A rapid circulation is thus maintained, and is greatly augmented when the water entering the tubes is so hot as to be converted into steam in the tubes. In a well-designed water-tube boiler a more efficient circulation is secured than in boilers of any other type—hence a reason why a more rapid supply of steam is procurable.

It is evident from all these examples that the property of convection in water is one of primary importance in the design of any type of boiler, and that, for a given heating-surface, the boiler in which circulation is best provided for will be the most efficient in practice. One of the chief drawbacks of defective circulation is the existence of different temperatures at different parts of the boiler, which is weakened by the strains thus caused; whereas if heated equally throughout strains are avoided.

Heating by Hot Water Circulation.—One of the commonest methods of warming a building is by the circulation of hot water from a boiler through pipes and special radiators. For domestic

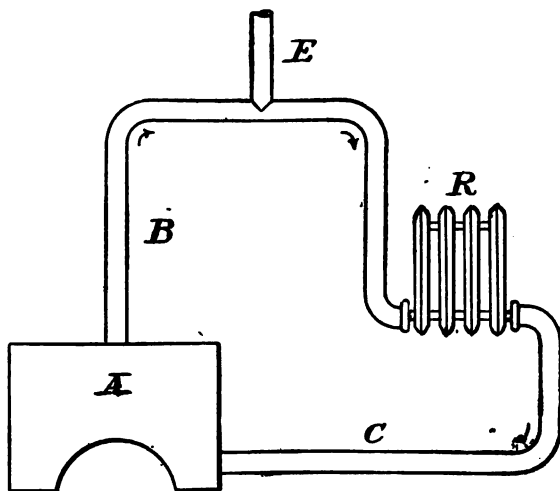


FIG. 92.—PRINCIPLE OF HOT-WATER CIRCULATION.

purposes a supply of hot water in various rooms is obtained by a similar system of circulation. The principle involved in each case may be understood by reference to Fig. 92, where A represents a boiler heated from below, from which convection currents of hot water rise through the pipe B, which enters the boiler at the top. After passing through the system of pipes, in the circuit of which radiators such as R may be placed, the water returns to the boiler through the pipe C, inserted at the lower end. The open pipe E serves to allow for the expansion of the water, and hence is termed an expansion-pipe.

The general arrangement of a hot-water system is shown in

Fig. 93. The hot water from the boiler B passes to a cylinder A, which serves to store a supply for tapping off. From the cylinder the circulation is continued by a pipe fixed to the top, from which side-branches are taken to radiators. At the highest part of the flow-pipe an expansion-tube E is fitted as a T-piece, so that the

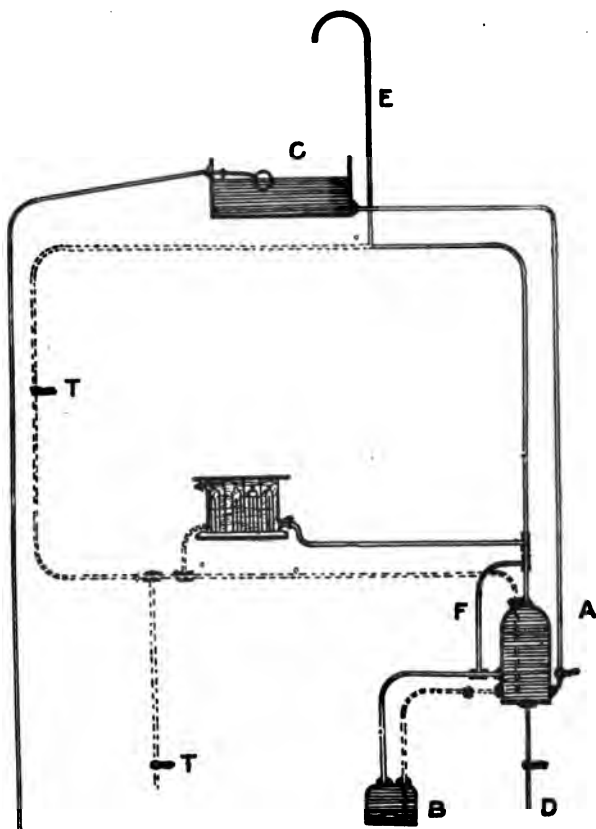


FIG. 93.—GENERAL ARRANGEMENT OF HOT-WATER APPARATUS IN A BUILDING.

system may be kept full of water without danger of rupture owing to expansion. The return-pipe is fitted at intervals with taps T, T, from which the hot water may be drawn off as desired for baths, lavatory-basins, etc. A better circulation is secured by drawing off from the return pipe than would obtain by using the flow-pipe for this purpose. The water from the return-pipe passes into the cylinder

A, and is discharged at the lower end, from whence it passes to the bottom of the boiler. The supply of water to the system is furnished by means of a cistern C, connected to the cold water supply, and furnished with a ball-cock. The lower end of this cistern is connected by a pipe to the bottom of the cylinder A, and when water is drawn off at any part an equal quantity enters from the cistern. When cold, the water will stand at the same level in the expansion pipe as in the cistern. An auxiliary flow-pipe F, connected as a branch to the hot-water entrance and exit of the cylinder A, serves to promote the circulation, and enables a more rapid supply of hot water to be available for the radiators, etc., than would be the case if the whole of the circulating water had to pass upwards through the cylinder, and heat up the large mass contained therein. The real function of the cylinder is to secure a reserve of hot water, which, on opening one of the taps, is driven into the pipes by the cold water entering at its lower end. For convenience in executing repairs, a stop-cock is placed near the cold-water entrance to the cylinder, which enables the supply to be cut off; and a drain-pipe D, communicating with the bottom of the cylinder, permits of the complete withdrawal of the water from the system.

Many modifications of the system described are in use; the differences, however, are in detail rather than principle. Any hot-water apparatus furnished with an expansion pipe open to the atmosphere is said to work on the "low-pressure" system, as distinct from the "high-pressure." In the latter case a continuous length of piping is used, bent into a coil at the fireplace, this coil serving as the boiler. At the highest level is placed an expansion chamber, having a capacity of about $\frac{1}{8}$ that of the entire system; and after the pipes have been completely filled with water the expansion chamber is hermetically sealed. The pressure in the interior may then rise to several atmospheres, with a consequent increase of temperature, as in the case of a steam-engine boiler. This system is sometimes used for heating rooms; being a closed system it cannot be used for furnishing a supply of hot water in addition. In some large hospitals the water is heated by exhaust steam from the engines used in connection with the electric lighting installation, and the hot water pumped through pipes and radiators placed in the various wards.

Length of Pipe required to Heat a Building.—The following formula, derived from practice, may be used to calculate the length of pipe, of given diameter, required to produce an assigned temperature under given conditions:—

Let P = temperature of pipes in degrees F.
 T = " required in building, degrees F.
 t = " of outside air, degrees F.
 C = cubic feet of air to be warmed per minute
 D = diameter of pipe in inches
 L = length of pipe in feet

Then

$$L = \frac{0.018 C (P - t) (T - t)}{D (P - T)}.$$

An example illustrating the use of this formula is appended.

Example.—To find the length of piping necessary to heat a room of 10,000 cubic feet capacity, the air of which is renewed 3 times per hour. Temperature of pipes = 150° F.; air in room, 65° F.; external air, 40° F.; diameter of pipes = 4 inches.

Applying values in formula

$$\begin{aligned} L &= \frac{(0.018 \times 500) \times (150 - 40) \times (65 - 40)}{4 \times (150 - 65)} \\ &= 73 \text{ feet.} \end{aligned}$$

(The air to be warmed = 30,000 cubic feet per hour = 500 per min.)

A few simple rules which lead to results not differing greatly from those obtained by the use of the formula are given below:—

1. To find the length of 4-inch pipe necessary to warm a room to 60° F., divide the cubic contents in feet by 150, when the quotient will give the length of pipe in feet. Thus, for a room of 10,000 cubic feet capacity, the length required is $\frac{10,000}{150} = 66\frac{2}{3}$ feet. If calculated

by the previous formula, the length indicated is 62 feet—a discrepancy less than that which might be caused by variations in the temperature of the outside air.

2. Three-inch pipes should be one-third longer, and 2-inch pipes twice as long as 4-inch pipes to heat the same space by the same amount. Or, generally, the length varies inversely as the diameter, as shown by the formula.

3. To secure an internal temperature of 65° F. in a dwelling-house, consisting of two or more storeys, allow 12 ft. of 4-in. pipe for each 1000 cub. ft. of space. This is in excess of that required for a single room.

4. In workshops 6 to 10 ft. of 4-in. pipe should be allowed for each 1000 cub. ft. of space.

All the above rules allow for the customary renewal of air by ventilation.

Calculation of Radiating Surfaces in Heating Buildings.—If the length of pipe obtained in the previous formula be multiplied by $2\pi r$, where r is the radius of the pipe in feet, the radiating surface necessary is obtained. Thus, in the foregoing example, where the length of 4-in. pipe necessary was found to be 73 ft., the radiating surface would be

$$73 \times 2 \times \frac{22}{7} \times \frac{1}{6} = 76.5 \text{ sq. ft.}$$

Another method of arriving at the result is as follows:—Measure up the surface of the walls and ceiling in square feet, exclusive of the glass of the windows, which is measured separately. Owing to its thinness, the glass allows of the greatest escape of heat by conduction, the loss through 1 sq. ft. being, on the average, equal to that escaping in this way through 10 sq. ft. of the remaining surface. Let T = temperature at which the room is to be maintained, P = temperature of pipes and t = temperature of outside air, all in Fahrenheit degrees, then the fraction $\frac{(T - t)}{(P - t)}$ = sq. ft. of radiating surface per sq. ft. of glass or its equivalent.

Example.—The dimensions of the room of a dwelling-house are $20 \times 15 \times 12$ ft., the window surface being 40 sq. ft. To find the area of radiating surface necessary to maintain a temperature of 65° F. when the temperature of the pipes is 150° F., and the outside air 40° F. The total area of the walls and ceiling is 1140 sq. ft., or, deducting that of the glass, 1100 sq. ft. Dividing by 10 the glass equivalent of the walls and ceiling = 110 sq. ft., and the total surface in terms of glass, = 150 sq. ft. From the formula $\frac{(T - t)}{(P - t)}$, the amount of radiating surface per sq. ft. of glass or equivalent surface = $\frac{(65 - 40)}{(150 - 65)} = \frac{5}{17}$ sq. ft.; and the total surface required = $150 \times \frac{5}{17} = 44$ sq. ft. This would be furnished by 42 ft. of 4-in. pipe. From Rule 3, for dwelling-houses, viz., 12 ft. of 4-in. pipe per 1000 cub. ft., the length calculated would be $(12 \times 3.6) = 43.2$ ft. length, as the contents = 3600 cub. ft. This is a practically identical result.

It is evident that any rule relating to pipe length or surface can only be approximate, as the heating effect is modified by the amount

of fresh air admitted, thickness of walls, extent of window surface, etc. When the installation is made by any of the foregoing rules, however, any deficiency or excess of heat can be remedied by increasing or diminishing the consumption of fuel in the furnace, thus raising or lowering the temperature of the pipes until the room is at the required temperature.

For the high-pressure system, the length or surface of pipes used may be approximated by taking $\frac{2}{3}$ of any of the results obtained as above.

Fire-Grate Area for Hot-water Circulation.—For a coal fire, with a good draught, 30 to 50 sq. in. of fire-grate area are required for every 100 sq. ft. of pipe surface. The larger figure leaves a safe margin for such contingencies as excessively low external temperature and frequent renewal of air.

Construction of Hot-Water Radiators.—In order to increase the area of the heated surface, radiators are interposed in the pipes conveying the hot water. They consist of a number of flat pipes placed side by side, and thus present a large surface to the room. The exterior should be coated with paint which presents a rough surface, colour being of no importance for heat waves of the non-luminous type. The radiating power is diminished considerably, however, if a metallic paint, giving a smooth surface, be used; hence the covering of radiators with aluminium paint—as is sometimes done for the sake of appearance—is a mistake.

Convection in Air. Winds.—When a mass of air is heated by contact with the warm surface of the earth, it rises, and is replaced by colder air, which, entering the vacated region with a noticeable velocity, gives rise to a wind. The velocity of the wind depends upon the difference of temperature of the heated air and that surrounding the heated zone, and in some cases may equal 100 miles per hour. Such a velocity, however, is rarely attained, and is nearly $\frac{1}{3}$ of the velocity with which air at 0° C. would rush into a vacuous space, viz., 743 miles per hour, or 1090 feet per second—a figure identical with the velocity of sound in air. In general, there is a tendency for air in the equatorial regions to rise, causing a flow from the poles towards the equator. This tendency is greatly modified by local circumstances, such as the distribution of land and water, many special winds such as monsoons, the sirocco, the mistral, etc., having a more or less local origin. It should be remembered that the rays of the sun do not heat the air in passing through, but warm the earth's surface on striking, so that any increase in atmospheric temperature arises from contact with the surface.

Draught of a Chimney.—The velocity with which a column of hot air will rise through a chimney may be calculated from Torricelli's theorem regarding the escape of fluids from an opening. According to this theorem, the velocity is given by the expression $V^2 = 2gh$, where h = head of fluid, and g the acceleration due to gravitation. The head of fluid giving rise to the upward pressure in this case is the difference between the height of the chimney, and the height to which a column of gas of the same section would extend when heated to the temperature existing in the chimney. Let H = height of chimney; T = temperature of air before heating, = atmospheric temperature, in absolute degrees; H_1 = height of column at the higher absolute temperature; T_1 = absolute temperature of hot gas in chimney, then

$$\frac{H_1}{H} = \frac{T_1}{T}, \text{ by Charles' law, and } H_1 = \frac{H T_1}{T}$$

The head of pressure is therefore

$$\frac{H T_1}{T} - H = \frac{H (T_1 - T)}{T}$$

and the velocity,

$$V = \sqrt{\frac{2 g H (T_1 - T)}{T}}$$

This formula is of little service in practice, as the friction on the sides, and varying temperatures at different heights of the chimney, alter the velocity greatly. It serves to show, however, that the velocity increases with the height, and also directly as the difference between the external and internal temperatures, and inversely as the external temperature.

A number of formulæ derived from practice are appended, which give results much nearer the truth than those derived from the above formula.

Let E = effective area = (actual area - allowance for friction),
in square feet

H = horse-power generated

A = actual area in square feet

S = side of square chimney in inches

D = diameter of round chimney in inches

h = height of chimney in feet

Then

$$\begin{aligned}
 E &= \frac{0.3 H}{\sqrt{h}} = A - 0.6 \sqrt{A} & . & . & . & 1 \\
 H &= 3.33 E \times \sqrt{h} & . & . & . & 2 \\
 S &= 12 \sqrt{E} + 4 & . & . & . & 3 \\
 D &= 13.54 \sqrt{E} + 4 & . & . & . & 4 \\
 h &= \frac{(0.3 H)^2}{E^2} & . & . & . & 5
 \end{aligned}$$

Before proceeding to examples involving these formulæ, it may be stated that it is assumed in them that each horse-power involves the consumption of 5 lb. of coal per hour, and that frictional losses are equivalent to the existence of a still layer of air 2 inches thick on each wall.

Example 1.—A circular chimney has a diameter of 5 feet = 60 inches. What height should it be made if used with a plant generating 500 horse-power?

$$\text{Actual area in square feet} = \frac{22}{7} \times (2.5)^2 = 19.65.$$

$$\text{Effective ditto from (1)} = 19.65 - (0.6 \times \sqrt{19.65}) = 17.$$

$$\text{From (5)} \quad h = \frac{(0.3H)^2}{E^2} = \frac{(0.3 \times 500)^2}{17^2} = 78 \text{ feet nearly.}$$

Or, approximately, 80 feet.

Example 2.—To find the horse-power which could be generated by a plant furnished with a square chimney, of 6 feet side, and 120 feet high.

$$\text{Actual area} = 36 \text{ square feet.}$$

$$\text{Effective area} = 36 - (0.6 \times \sqrt{36}) = 32.4.$$

$$\text{From (2)} \quad H = (3.33 E \times \sqrt{h}) = 3.33 \times 32.4 \times \sqrt{120} = 1182, \text{ or roughly } 1200.$$

In determining the dimensions of a chimney, due regard must be paid to the locality in which it is erected. If on a hill, open to winds, a less height will be necessary than when in a sheltered situation. The following table shows the heights given to chimneys under average circumstances, when intended for the consumption of a given quantity of good coal. The horse-power may be determined by dividing the coal burnt by 5. If inferior fuel be used, a greater height is requisite, and to burn anthracite slack to advantage a minimum height of 175 feet is necessary.

HEIGHT OF CHIMNEYS.

Height in Feet	Pounds of Coal Burnt per Hour in Chimney of Actual Diameter (feet)													
	1 ft.	1'5	2'0	2'5	3'0	3'5	4'0	4'5	5'0	5'5	6'0	7'0	8'0	9'0
60	46	141	287	485	735	1040	1390	1800	2250	2760	3320	4610	6080	7700
80	331	561	850	1190	1600	2070	2600	3180	3830	5320	6990	8900
100	950	1340	1790	2320	2810	3550	4290	5940	7810	9950
125	2000	2580	3250	3960	4790	6640	8730	11100
150	2830	3560	4350	5240	7290	9570	12150
175	3860	4720	5690	7900	10490	13200
200	5010	6050	8410	11100	14100

Draught of a Chimney in Terms of a Water-Column.—A water-column furnishes a convenient means of expressing the draught of a chimney. If the end of one limb of a glass U-tube be bent so as to pass into the chimney, and water be poured into the tube, it will rise to a higher level in the limb connected with the chimney, owing to the diminished pressure caused by the upward rush of gases. The difference of level observed in the two branches expresses the draught in terms of a column of water. This is a convenient method of testing the efficiency of a chimney under working conditions. The following formula is useful for calculating the draught that should be given by a chimney of given height :—

$$D = H \left(\frac{4 \cdot 22}{T} - \frac{4 \cdot 39}{T_1} \right)$$

where D = draught in inches of water

H = height of chimney in feet

T = absolute temperature of air in degrees Centigrade

T₁ = absolute temperature of gases in chimney in degrees Centigrade.

If temperatures on the Fahrenheit scale be used, the formula is

$$D = H \left(\frac{7 \cdot 6}{T} - \frac{7 \cdot 9}{T_1} \right)$$

the symbols T and T₁ representing absolute degrees, which on the Fahrenheit scale = (ordinary degrees + 460).

Example.—To find the draught, in inches of water, given by a

chimney 100 feet high, when the temperature of the air is 10°C. or 50°F. , and the temperature of the gases in the chimney is 160°C. or 320°F.

Applying in formula

$$D = 100 \left(\frac{4 \cdot 22}{283} - \frac{4 \cdot 39}{433} \right) = 0 \cdot 48 \text{ inch}$$

$$\text{or, in deg. F, } D = 100 \left(\frac{7 \cdot 6}{460 + 50} - \frac{7 \cdot 9}{460 + 320} \right) = 0 \cdot 48 \text{ inch.}$$

In a practical determination the temperature of the furnace gases can be obtained from the readings of a pyrometer placed in the chimney.

Another simple rule is as follows:—"To find the maximum draught for a chimney when the temperature of the air is 62°F. , and of the hot gases 600°F. , multiply the height of the chimney above the grate by $\cdot 007$." The answer is given in inches of water, and in the case of a chimney 100 feet high would therefore be $\cdot 7$ inch.

Weight of Gases Ascending Chimney.—The gases escaping from a chimney consist of carbon dioxide, carbon monoxide, steam, nitrogen, and unused oxygen. As these gases have different densities, it is evident that the weight escaping in a given case depends upon the relative amount of each present. For chimneys over 3 feet in diameter, under normal conditions, the weight is given approximately by the formula

$$\text{Weight in lb. per second} = 85 \times \frac{A}{T_1} \times \sqrt{\frac{h(T_1 - T)}{T}}$$

where A = actual area in square feet, h = height of chimney in feet, T_1 = absolute temperature of hot gases in degrees F., and T = absolute temperature of air in degrees F.

Example.—The weight of escaping gases for a chimney of area 16 square feet, height 100 feet, with hot gases at 300°F. and air at 60°F. , would be 12.12 lb. per second, as calculated by the above formula.

If a series of weights be calculated for a chimney of given dimensions from the above formula, taking the temperature T of the outside air as constant, and varying T_1 , it will be found that the weights increase rapidly up to a point where T_1 exceeds T by 200°F. , after which the increase is slower, and finally a maximum is reached beyond which a further increase in T_1 shows a diminishing weight of gases escaping. This is shown graphically in Fig. 94, in which pounds per

second are plotted against the difference of temperature between the hot gases and surrounding air, or $(T_1 - T)$, in a chimney of given dimensions. It will be seen that the maximum occurs when $(T_1 - T)$ is equal to about 550°F. , so that if the air were at 60°F. , any increase in temperature in the chimney above 610°F. would result in a less weight of escaping gases. The maximum, moreover, is only slightly in excess of the weight corresponding to $(T_1 - T) = 300^\circ \text{F.}$, and hence it is desirable to reduce the temperature of the escaping gases to a point where $(T_1 - T) = \text{about } 300^\circ \text{F.}$, to ensure economic working. In this connection it should be remembered that the rate of combustion is determined by the weight of air passing

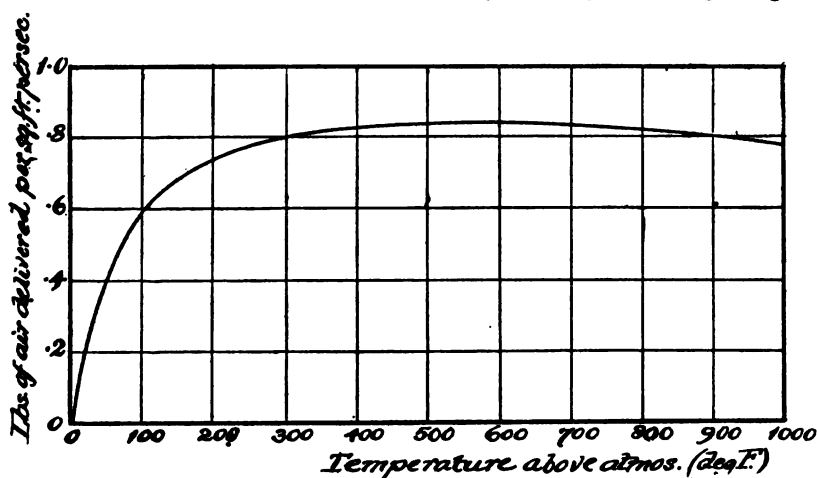


FIG. 94.—CURVE SHOWING WEIGHT OF AIR PASSING UP A CHIMNEY AT DIFFERENT TEMPERATURES.

through the fuel, and that the hotter the escaping gases, the greater will be the loss of heat in the chimney. The reason why a point of maximum efficiency is reached will be understood from the fact that the weight of one cubic foot of gases diminishes directly as the absolute temperature, whilst the velocity increases only in the ratio (approximately) of the square root of the absolute temperature, and hence fails, after a certain point, to compensate for the diminished density.

Ventilation.—The problem of renewing the air in rooms, embraced by the term “ventilation,” involves in most cases the property of convection in air. Successful ventilation, however, is by no means a simple matter, and a system satisfactory for one building may prove

a failure for another differently constructed and situated. The subject covers a wide ground, and it will only be possible to deal with the general principles involved, within the limits of the present treatise.

Ordinary fresh air contains 4 parts in 10,000 of carbon dioxide, and in a room occupied by human beings, each exhaling 0.6 cubic feet per hour, the proportion of CO_2 rises considerably unless the air be frequently renewed. Ideally, the proportion of CO_2 should never exceed 6 parts in 10,000, which means that every adult should have a breathing space of 3000 cubic feet per hour, or 1000 cubic feet renewed three times per hour. The carbon dioxide itself is not injurious, but serves by its amount to furnish a clue to the quantity of organic matter present, which gives rise to "stuffiness" in a room, this effect being enhanced by the excess of moisture resulting from exhalation. In practice this ideal cannot, for various reasons, be attained, as to secure 3000 cubic feet of space per adult would involve buildings of absurdly excessive size, and to renew the air of a room in this country more frequently than three times per hour involves the creation of draughts, which, besides being uncomfortable, may cause more injury than slightly-vitiated air. No harm results in most cases from remaining for short periods in a room containing far more than 6 parts in 10,000 of CO_2 ; but ill-effects are noticeable in all cases where a stuffy atmosphere is persistently breathed.

A general idea of the space allowed per head may be obtained from the following selected examples, the minimum usually being prescribed by Government regulations:—

	Cubic Feet per Head
Dwelling-houses	1000
Common lodging-houses	300 (minimum)
Poor Law Boards	300 „
„ sick persons	850 to 1200
Factories and workshops	250 (minimum)
„ „ overtime	400 „
Army, regulation space	600
London schools (County Council)	130 (minimum)
Hospitals, ward space	2000 „

In addition to cubic contents, it is necessary to prescribe a minimum for floor space. A room 20 feet long by 15 feet wide and 10 feet high, would possess the same cubic contents as another 15 × 10 × 20 feet high, but the latter would be much inferior in respect to an easy renewal of air. The minimum allowance for floor space is expressed in square feet by dividing the contents in cubic feet by 12. Thus a room of 1200 cubic feet capacity should have a

minimum floor space of 100 square feet, and would be better, for ventilating purposes, with a floor space of 120 square feet.

The rate at which the air in a room may permissibly be removed depends upon the sensitiveness of the occupants to draughts. The incoming air, when cold, should not on this account exceed $2\frac{1}{2}$ feet per second in velocity, or 3 feet per second when warm. It is this factor which places a limit on efficient ventilation.

"Natural" Ventilation.—This term is intended to include all systems of ventilation in which the renewal of air is effected without the aid of mechanical appliances, such as exhaust-fans, etc. The expired air from individuals is at the temperature of the human body— 98° F. or $36\cdot5^{\circ}$ C.—which is greater than the temperature existing in a room in this country, even in the hottest weather. Consequently the warm gases exhaled rise through the colder air of the room, and if an outlet be provided at a high level, together with an inlet for cold air at a lower level, the expired gases will escape above and be replaced by an equivalent quantity of pure air below. If an outlet only is provided, no circulation is set up, as this would entail the cold air entering at the same time and place as that at which the warm air escapes, one tendency counteracting the other. It is evident that the rate at which the air is renewed in this way depends upon the speed at which the warm gases rise and escape, and this in turn is determined by the difference of temperature between the warm gases and the air of the room. Hence a low temperature in the air of a room favours an efficient renewal of the air; but to secure comfort to the occupants this temperature should not fall below 65° F. The velocity with which the gases commence to ascend is consequently that due to a difference in temperature of about 35° F., or about 5 feet per second; but as the warm gases rise diffusion takes place with the colder air of the room, and the velocity falls off considerably. In a lofty room this diffusion is complete before the upper portion is reached, the result being to establish a stagnant layer of warm air in this region. It is evident, therefore, that the automatic tendency to renew the air is considerably hampered, and cannot in itself be relied upon to secure efficient ventilation except under very favourable circumstances.

Gas-jets burning in a room produce carbon dioxide and water, each jet consuming as much oxygen as three adults. The products of combustion are non-injurious when mixed with sufficient air, and with a properly arranged outlet and inlet the burning of gas-jets assists greatly in renewing the air of the room. The products rise from the jet at an extremely high temperature and consequent high

velocity, and reach the outlet before diffusion has taken place to any great extent. A strong escaping current is thus established, and a renewal of the air of the room results in consequence. In many cases the improved ventilation thus obtained more than compensates for the impurities introduced by the combustion of the gas, owing to the non-existence of a stagnant upper layer of air. For this reason the air of rooms illuminated by gas is frequently less vitiated than is the case when electric lighting is adopted, especially when occupied by a number of people.

The renewal of air effected by opening the windows of a room takes place in different ways, according to circumstances. If there be no fireplace in the room, and a window be opened at the top, the warmer portions of the air will escape through the window, and be replaced by air entering under the door, or through any other inlet at a lower level. If, however, the room be furnished with a fireplace, the air of the room tends to rise up the chimney, owing to the wind blowing across the exit at the roof; and in this case the open window will serve as an inlet. This effect is greatly increased when a fire is burning in the grate, the hot gases rising up the chimney causing a rush of air from all inlets towards the fireplace. Experience shows that a room in which a bright fire is burning is generally well ventilated. In warm weather the renewal of air is best effected by throwing open the windows and doors, and allowing a current of air to blow through the rooms. If the current be too strong for comfort, closing the door of a room, and opening the windows both at the top and bottom, will enable ventilation to take place.

In many cases it is not found possible to secure the desired renewal of air by means of windows, etc., and recourse must then be had to special fittings for this purpose, some of which will now be described.

The Sherringham Valve.—This arrangement, as shown in Fig. 95, consists of a V-shaped iron box, hinged at its lower edge, which is let into the wall to serve as an inlet. It can be opened to any desired extent by means of a cord passing over pulleys, and furnished with a counter-weight. The incoming air is directed upwards, so as to avoid creating a draught in the occupied part of the room.

Tobin's Tube.—In this method of air admission (Fig. 96), a tube running parallel with the wall is furnished with a right-angle bend which passes through the brickwork to the exterior, the entrance being guarded by an iron grating. As in the previous device, the entering air is directed upwards.

Air Bricks.—Entrance of air is sometimes obtained by the use

of perforated bricks, the holes through which the air enters the room being inclined upwards to avoid draughts.

Chimney Breast Valves.—The chimney of a room furnishes a convenient exit for vitiated air, and many arrangements are in use to permit of this method of escape. An opening is made in the flue near the ceiling, in which is placed a hinged valve of metal or mica, which lifts sufficiently to permit of the passage of the gases at the top of the room, owing to the diminished pressure generally existing in the air of a flue. Back action, caused by the air in the flue for some reason attaining a superior pressure, is prevented by

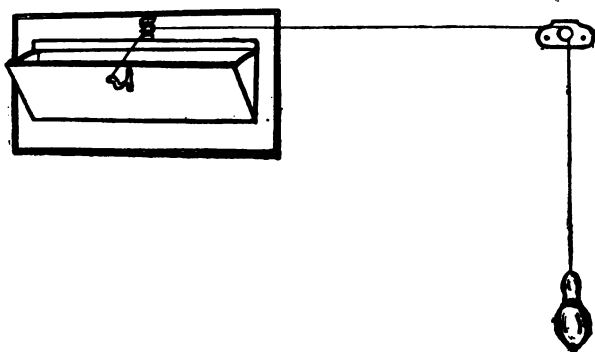


FIG. 95.—SHERRINGHAM VALVE.

means of a stop, against which the hinged valve is urged, thus closing the opening. A grid-iron front to the valve-box enables the extent to which the gases escape to be controlled.

Arrangements for Heating entering Air.—Many arrangements are in existence for the purpose of warming the entering air by means of the heat generated by the fire in the room. The duct conveying the incoming air is made to pass in the vicinity of the fireplace, thus causing the air to be warmed before delivery into the room, the temperature of which is thus maintained with a smaller consumption of fuel than would otherwise be the case.

"Artificial" Ventilation.—The utilisation of the ordinary fixtures of a building, even when assisted by the addition of special outlets and inlets, frequently fails to secure an adequate supply of fresh air to the various rooms. In such cases it is customary to remove the air by exhaust-fans or by propulsion, the supply of fresh air being admitted by suitable inlets. As the quantity of air admitted may be regulated at will, and also purified or moistened if requisite, this would appear to be a more certain way of renewing the air of a

room than by employing "natural" methods only. In practice, however, the results anticipated are seldom realised, and in some cases costly installations have been abandoned as useless. The reasons for the failures experienced are somewhat obscure, but

may probably be summed up by the statement that—except in rare cases—the whole of the air of a room cannot be continuously driven towards an exit without creating unpleasant draughts. In the case where an exhaust-fan is used to remove the vitiated air, for example, there is a tendency for a direct current to set up between the fan and the inlet, leaving the air in other localities practically stagnant. A judicious arrangement of a number of inlets at different parts of the room will minimise this difficulty, but even then it is necessary that the currents should continually pass amongst the occupants of the room, who, in most cases, object to the draught created, and close the offending inlet.

In some cases the vitiated air is extracted by steam-jets, water-jets, or by a fire burning in a specially-constructed shaft. Generally speaking, the impure air of a building can be removed better by extraction than by methods in which propulsion is used, where the fresh air forced in is relied upon to expel that already present in the room.

The difficulties attendant on the ventilation of large buildings successfully are illustrated in the many attempts made in connection with the Houses of Parliament. The debating chamber in the House of Commons has been made the subject of many experiments in ventila-

tion, but none have proved quite satisfactory. As arranged at present, the air is extracted by means of a ventilating shaft, at the bottom of which a coke fire is kept burning. The incoming air is driven in by means of a fan, which supplies the air at a somewhat greater rate than would compensate for the exhaustion caused by the fire in the shaft, and consequently the air in the chamber is at a slightly higher pressure than that existing in the corridors. In summer the fresh air supply is washed and cooled before admission, in winter it is warmed by passing over steam-heated

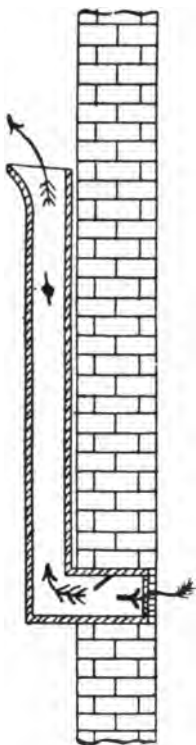


FIG. 96.—TOBIN'S
TUBE.

surfaces. Inlets for the fresh air are provided on the floor of the chamber and elsewhere, but all these elaborate arrangements do not succeed in continuously renewing the air at all parts of the chamber, and when crowded with members the inadequacy of the installation in this respect is manifest. The various schemes applied to hospitals, etc., in which artificial ventilation has been adopted, have generally fallen below expectations owing to the inherent difficulty of completely renewing the air without creating objectionable draughts.

Size and Arrangement of Inlets.—When the velocity of the entering air is known, the size of opening requisite to secure a complete renewal of the air in the room may easily be calculated. If, for example, the air in a room of 1000 cubic feet capacity requires to be changed 3 times per hour, it will be necessary to admit at least 3000 cubic feet per hour to effect this renewal. If the velocity of the incoming air be 3 feet per second, and the size of the opening be x square feet, the quantity of air entering per second will be $3x$ cubic feet, and per hour $3 \times 3600x = 10800x$ cubic feet. Hence the area of the inlet necessary to admit 3000 cubic feet per hour = $\frac{3000}{10,800} = \frac{1}{3.6}$ square feet = 40 square inches.

In practice it is necessary to make a greater allowance than is indicated by the calculation, as the velocity of the entering air may vary considerably, being greater when the outside temperature is relatively low, and when assisted by winds, and less with a high external temperature and in the absence of wind. The quantity admitted is also influenced by the nature of the inlet, owing to friction in the entrance-pipe or grating. It is therefore advantageous to allow a liberal margin above the calculated size, and to control the quantity admitted by altering the size of the inlet, which should be constructed so as to permit of regulation.

In ventilating mines, and in all cases where the air is forced through pipes or ducts, the head of pressure necessary to generate by means of the fan or blower may be obtained from Morrison's formula, which is as follows :—

$$H = \frac{K V^2 P L}{A}$$

where K = Coefficient of friction = .03
 V = Velocity of air in thousands of feet per minute
 P = Perimeter of cross-section in feet
 L = Length of duct in feet

A = Area of duct in square feet

H = Head in feet of pressure of air of same density as entering air.

For a circular section, of diameter D , the perimeter $P = \pi D$, and the area $A = \frac{\pi D^2}{4}$.

Hence

$$\frac{P}{A} = \frac{\pi D}{\frac{\pi D^2}{4}} = \frac{4}{D}$$

and hence the formula, for a duct of circular section, becomes

$$H = \frac{K V^2 4L}{D}.$$

Example.—The head of air pressure necessary to deliver air at 5 feet per second = .6 of a thousand feet per minute, through a duct of square section, 1 foot side and 200 feet long, is

$$\frac{.03 \times .6^2 \times 4 \times 200}{1} = 8.64 \text{ feet.}$$

In arranging inlets, due regard to position in the room must be observed, so that the incoming air is breathed by the occupants before mixing with vitiated air, and draughts avoided. A better distribution is secured by the use of a number of small inlets in preference to one or two large ones.

Use of Electric Heaters in Rooms.—Many types of stoves are now in use in which the heat is furnished by electricity: a favourite form consisting of a number of glow-lamps placed in front of a metallic reflector, so as to imitate the brightness of a coal fire. It is claimed for these that the extra cost of the electricity is compensated for by the fact that all the heat generated is utilised in warming the room, whereas in the case of a coal fire the major portion of the heat—60 to 80 per cent.—escapes through the chimney. This claim cannot be substantiated, as 6 pounds of coal, costing 1 penny, will furnish 80,000 B.Th.U., and if the chimney loss be 80 per cent., 16,000 B.Th.U. are still available for warming the room. The heat equivalent of 1 Board of Trade unit of electricity is 3400 B.Th.U. and hence at the low price of 1 penny per unit electric heaters are far more costly than a coal fire. Even if the contrary were true, the

ventilating effect of a coal or gas fire would still render this mode of heating preferable to electricity for domestic use, as from this standpoint the heat escaping up the flue is not lost, but fulfils a function as useful as the actual warming of the room. The real points in favour of electric heaters are cleanliness, and the ease with which the supply of heat may be switched on and off, and regulated as desired.

CHAPTER XIX.

THE TRANSFER OF HEAT. RADIATION.

Heat Waves.—Any objects placed in the vicinity of a body at a higher temperature will be found to undergo a rise in temperature, even though a vacuum should separate them from the source of heat. The energy transferred in this manner through an intervening space, without the aid of conduction or convection, is termed “radiant” heat, and represents energy transmitted by ether waves. It may be shown in many ways that heat waves possess properties identical with light waves; thus, for example, heat waves are capable of reflection, refraction, and polarisation. Every substance at a temperature above absolute zero acts as a source of heat waves, that is, gives rise to undulations in the ether; and the higher the temperature the greater is the disturbance created, and the greater also is the quantity of energy leaving the substance in a given time. Hence if a number of bodies at different temperatures be placed in a room, the tendency of radiation is to establish an equal temperature in all, as the hotter bodies lose heat energy more rapidly than the colder ones. All radiate heat to each other, with the result that the hotter bodies lose more heat than they receive, whilst the colder bodies gain more than is radiated by them. Finally, when each body receives from its surroundings just sufficient heat to balance that which is radiated from it, equality of temperature has been attained. For like reasons a block of ice—apart from air convection—cools everything in a room, as the heat radiated from the objects to the ice is not returned in equal amount by the ice.

Absorption of Heat Waves.—The heat waves which impinge on a given object are partly thrown back by reflection, and partly absorbed, that is, utilised in imparting an increased kinetic energy to the molecules, a rise in temperature occurring in consequence. The facility with which heat energy is thus absorbed, and also with which it is given off by a substance, depends upon the nature of the surface which receives or sends off the heat waves, as will now be shown.

Effect of Surface on Radiation and Absorption.—It is well known

that hot water will take longer to cool when stored in a vessel with a smooth, metallic surface than when contained in a receptacle with a rough surface. Conversely, if cold water be placed in a vessel with a polished surface in front of a fire, it will take longer to become heated than if the surface were rough. The retention of heat by a polished surface is due to the relatively small amount of radiation which takes place; and the slow heating, when placed near a source of heat, is due to the small absorbing power. In each instance the reflecting power of the surface is the determining factor; the heat passing from the hot water to the polished surface being reflected back to a large extent in the one case, and cooling thus delayed, whilst in the other case the heat waves falling externally on the surface are in the main reflected back, only a small portion being absorbed and a slow heating resulting in consequence. A good reflecting surface is therefore not capable of radiating or absorbing heat waves to any great extent, but a rough surface, which has little reflecting power, will radiate or absorb freely. A surface which possessed no reflecting power, and which was opaque to heat waves, would absorb the whole of the radiant heat it received externally, and, conversely, would radiate completely any heat reaching it from beneath. No such surface is known, the closest approximation being given by lamp-black, which is superior to any other surface both with respect to radiation and absorption of heat waves in general. It will be shown later that for non-luminous or dark heat waves, other rough surfaces are practically equal in these respects to one of lamp-black, but are much inferior for luminous heat waves.

It will be seen from the foregoing that the polished brass dome of a locomotive assists in the retention of heat, and is preferable to a rough surface; and also that the polishing of the cranks, connecting-rods, etc., causes them to reflect radiant heat from the boiler and cylinders and so to remain cool. A silvered tea-pot or other vessel will keep a liquid hot for a longer time than one with a rough surface, and a steam-pipe lagging is more efficient when finished with a smooth varnished surface than if left rough.

The Absolute "Black Body."—Although no known surface acts as a perfect radiator or absorber of heat, it is possible, as Kirchoff showed, to make an arrangement which will give radiations equivalent to those received from a perfect radiating surface. Such an arrangement is termed a "black body," and the radiations obtained from it are known as "black-body" radiations. The necessary conditions are fulfilled by the radiations received from the interior of an enclosure kept at a constant temperature in all its parts. Such an enclosure is

represented in Fig. 97, and if the temperature be equal throughout, the radiations received through a small opening in the side from the surface of A will be independent of the nature of the surface. For if A possess a perfect radiating surface, rays falling upon it from the enclosure will be entirely absorbed, and hence, as its temperature remains constant, the surface will radiate an amount equal to that received. If, on the other hand, the surface of A be not perfect, some of the heat rays falling upon it from the enclosure will be reflected, and the remainder absorbed. Equality of temperature, however, involves the condition that the heat leaving the surface is equal to the amount received, and as the heat incident upon A from the enclosure will be the same, whatever the nature of the surface, it follows that the heat leaving A is constant under the given conditions. Hence the amount of heat received from A through a small opening

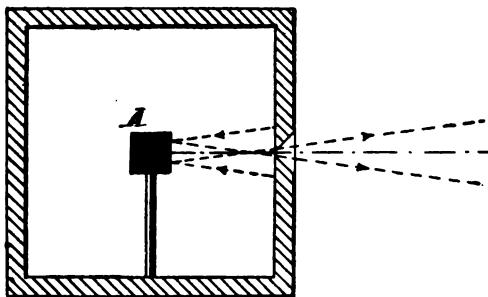


FIG. 97.—“BLACK-BODY” RADIATIONS.

in the side will be independent of the surface, as the constant temperature condition ensures that the heat leaving the surface is a fixed amount. Further, this amount is equal to the total radiations received by A from the enclosure, and hence the surface of A is equivalent to a perfect radiating surface, which would absorb all heat falling upon it and radiate an equal amount if its temperature were unchanged.

In practice, a black body may be obtained in the manner indicated in Fig. 97, the box being packed in ice, or kept in a bath at constant temperature. A body placed in the interior of a tube heated externally will similarly give black-body radiations through the open end when the temperature is constant. A block of steel in a furnace, the temperature of which is steady, also gives black-body radiations through a hole in the side of the furnace. In each case the imperfection of the surface as a radiator is counterbalanced by the reflection of rays received from the enclosure, which pass through the opening

and make good any deficiency in the radiant heat proper. If outside the enclosure, the heat received from the surface would be less by the amount of these reflected rays. A lamp-black surface in the open radiates nearly as well as a black body, whilst smooth surfaces are greatly inferior.

Connection between Quantity of Heat Radiated and Temperature.—Newton, who was the first to investigate this subject, came to the conclusion that the heat lost by a body, when cooling under uniform conditions, was proportional to the difference between the temperature of the body and that of its surroundings. Thus, for a given substance at 210°C . and 110°C . respectively, cooling in surroundings at 10°C ., the rates of cooling would be as $(210 - 10) : (110 - 10) = 2 : 1$. Although this law is approximately true for small differences of temperature—say 20°C .—it is greatly in error when the differences are large. Dulong and Petit, and others, arrived at formulæ from experiments conducted under known conditions, and by the use of these formulæ a more correct result than that derived from Newton's law could be obtained. The correct law was announced by Stefan in 1879, and was later confirmed theoretically by Boltzmann. The Stefan-Boltzmann law states that the energy radiated by a given body is proportional to the fourth power of its absolute temperature, and expressed in symbols takes the form

$$E = K (T_1^4 - T_2^4)$$

where E = total energy radiated; T_1 and T_2 the absolute temperatures of the body and its surroundings respectively, and K = a constant. The law is only strictly true for black-body radiations, for which the constant K will depend upon the units chosen. For an ordinary body radiating heat, the constant K will depend also on the radiating surface; thus a lamp-black surface, at the same temperature, would radiate more energy than one of silver. Under black-body conditions the nature of the surface makes no difference, as previously shown.

The application of the above law to pyrometry will be found in Chapter VIII.

The rate at which a body cools in air depends not only upon the nature of the surface and the temperature, but also upon the specific heat. If, for example, 1 calorie be extracted from 1 gram of aluminium (specific heat $\cdot 23$) the fall in temperature occasioned will be

$\frac{1}{\cdot 23}$ or $4\cdot 4^{\circ}\text{C}$., whilst 1 calorie taken from 1 gram of iron (specific heat $\cdot 11$) will lower the temperature by $\frac{1}{\cdot 11}$ or 9°C . If two surfaces

of different metals possess the same radiating power and area, the rates of cooling will be proportional to the specific heats of the metals compared by volume, when both are cooled from the same temperature. In the case of a single substance, the rate at which the temperature falls depends upon the mass, the nature of the surface, and the absolute temperature—the energy radiated, even for an imperfect surface, being nearly proportional to the fourth power of the absolute temperature. A mass of hot substance, cooling in air, also loses heat by convection, hence the fall in temperature will be more rapid than that calculated from the radiation constants only. In a large mass of material, the rate of cooling is influenced by the conductivity, which determines the rapidity with which heat from the interior reaches the surface. The rate of cooling will evidently be more rapid when the temperature of the surrounding atmosphere is low, as may be seen from the symbolic expression of the Stefan-Boltzmann law, which indicates that a diminution in T_2 causes an increase in the energy lost by radiation.

Instruments for Detecting Radiant Heat.—In radiant heat investigations it frequently occurs that small differences or alterations in temperature, not detectable by an ordinary thermometer, require to be noted. The employment of a large-bulb mercury thermometer with a narrow bore is in general unsuitable in these cases, as the incident heat is usually small in quantity, and would not suffice to heat up a large mass of mercury. Any instrument, therefore, to be of service in this respect, must possess a low thermal capacity; that is, a slight quantity of heat energy must be capable of producing a rise of temperature sufficient to be indicated by the instrument. The methods available at present comprise (1) differential air thermoscopes, used for comparatively rough indications; (2) thermopiles, for more delicate observations; and (3) the bolometer, (4) the radio-micrometer, and (5) the suspended-vane radiometer, for detecting excessively minute temperature changes. Each method will now be described in turn.

The Differential Air Thermoscope (sometimes called Thermometer). This instrument, invented by Leslie, is shown in Fig. 98. It consists of a tube with a bulb at each end, bent so as to form two parallel branches. The bore of the tube contains a quantity of coloured liquid which serves as an index, and in good forms of the instrument the parallel branches are connected by a cross tube, furnished with a tap, which, on being opened, equalises the air-pressure in the bulbs, and causes the index-liquid to stand at the same level in both branches of the tube. On closing the tap, and subjecting one of the bulbs to

a slight rise in temperature, the index liquid will be forced down in the branch of the tube connected to the heated bulb, and will rise in the other. As air has a high coefficient of expansion, a slight rise in temperature will produce a marked depression of the liquid. The thermal capacity of the air-bulb, moreover, is small, hence the application of a small quantity of heat will cause a notable rise in temperature. This instrument was used by Leslie in studying the phenomena of radiant heat.

In more modern forms of the instrument, the bulbs are connected to the index by flexible tubing, and hence may be placed in baths or any desired place. Bulbs with re-entrant portions are also made, so as to contain a liquid; and thus such heat changes as that occasioned

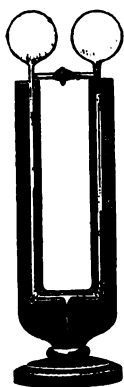


FIG. 98.—DIFFERENTIAL
AIR THERMOSCOPE.



FIG. 99.—THERMOPILE.

by dissolving a small quantity of sal-ammoniac or other salt in water, may be readily detected. Many useful indications may be obtained with this improved form of thermoscope.

The Thermopile.—This instrument, due to Melloni, is a much more sensitive heat-detector than the air thermoscope. It consists of a number of junctions of antimony and bismuth, arranged in series, and collected together in a compact form so that all the junctions lie close together, as shown in Fig. 99. Melloni used this arrangement, in connection with an astatic galvanometer, for conducting his experiments on radiant heat. In conjunction with a mirror galvanometer, the thermopile is far more sensitive, and will indicate a very minute rise in temperature. Antimony and bismuth were chosen, as a

heated junction of these two metals gives a relatively large E.M.F., and when a number are placed in series, the total electromotive force is the sum of the E.M.F.'s generated at each junction. Hence a small rise of temperature is sufficient to give a marked indication on the galvanometer.

The chief defect of the antimony-bismuth thermopile is that it possesses a high thermal capacity, and when once heated takes a long time to cool to its original temperature. This feature greatly impairs the sensitiveness of the thermopile, when used for detecting changes in which the quantity of heat is small. Both the metals are too brittle to be drawn into fine wires, and must possess considerable bulk in order to be worked satisfactorily. The so-called "linear" thermopile, devised by Rubens, is in this respect a great improvement on the old form. The junctions (of copper and constantan, or iron and constantan) are made of fine wire, and are hammered flat so as to present a large surface to the source of heat. A very large number of these junctions, joined in series, are brought close together, and it is thus possible, in a given size of thermopile, to obtain a higher E.M.F. than when a necessarily smaller number of antimony-bismuth junctions are used, whilst the thermal capacity is very small. The linear thermopile is well suited to such observations as the distribution of heat in the spectrum, and in all cases where the quantity of heat received by the instrument in a given time is small. The flattened junctions should be coated with lamp-black, in order that heat radiations falling on them may readily be absorbed.

The Bolometer.—The increase in the electrical resistance of platinum when heated has already been referred to in connection with the resistance pyrometer, and the same principle is applied in the delicate heat-detector devised by Langley, and known as the bolometer. A grating of thin platinum foil, each strip of which has dimensions about 1 cm. long, $\frac{1}{2}$ mm. wide, and $\frac{1}{100}$ mm. thick, is blackened on its upper surface, and placed in one arm of a Wheatstone bridge. This grating may be covered up or exposed to the heat source as required, and, in taking an observation, the adjustable arm of the bridge is altered until no deflection of the galvanometer occurs on depressing the keys, the grating meantime being shielded from the source of heat. The grating is now exposed, and if its temperature increases, its resistance also will increase, and on closing the circuit the galvanometer will show a deflection. With resistance coils of sufficient delicacy the increase may be measured, and the rise in temperature deduced. By using the most refined methods of measuring electrical resistance, Langley was able to

detect a difference of $\frac{1}{10000}$ of a degree Centigrade in the temperature of the grating. The chief advantage of the bolometer is the small quantity of heat required to raise the temperature of the grating, as the weight of the thin foil is extremely small, and the specific heat of platinum very low. The amount of heat required to raise the temperature of a grating composed of 10 strips, of the dimensions given, by 1°C. , is less than $\cdot 00007$ of a calorie; and in this respect the bolometer is greatly superior to the thermopile. In measuring the resistance, it is necessary to pass a current through the grating, which, although momentary, will cause its temperature to rise. By placing an exactly similar grating, constantly shielded, in another arm of the bridge, so as to counterbalance the other when both are at the same temperature, any discrepancy due to this cause is avoided, as the current will affect both equally. By the aid of the bolometer, Langley carried out a series of important investigations connected with the distribution of heat in the spectrum.

The Radio-Micrometer.—When a current of electricity is passed through a coil of wire suspended in a magnetic field, the coil turns either to the right or the left, according to the direction of the current. This principle is applied to the construction of sensitive galvanometers, and d'Arsonval constructed a detector of radiant heat in which the current through the coil was furnished by a small thermal-couple, on which the heat rays impinged, and which indicated any alteration in temperature sustained by the junction by the movement of the coil. Later, and independently, Professor Boys devised an extremely sensitive instrument, working on the same principle, to which the name of radio-micrometer was given. The working of the instrument may be understood by reference to Fig. 100. The coil consists of a thin loop of copper wire, suspended by a quartz fibre, and joined at one of its extremities to a thin piece of antimony, and at the other to a similar piece of bismuth. The antimony and bismuth are each soldered to a thin disc of copper, which has a blackened surface; and the coil hangs between the poles of a powerful magnet. A mirror is attached to the suspension, upon which a spot of light is thrown and reflected on to a scale, thus magnifying the movements of the coil. So long as the circuit formed by the loop and the thermal couple is at the same temperature throughout, no current will flow through it; but the slightest alteration in the temperature of the copper disc, to which the antimony-bismuth couple are fastened, will give rise to a current in the circuit, and the loop will twist on its suspension owing to the mutual action between the current and magnetic field.

In the actual instrument, the parts are covered in so as to be screened completely from radiations. Opposite the blackened copper disc is a metal tube furnished with a cap, which enables the heat received from any source to be tested by removing the cap, and allowing the radiations to impinge on the copper disc to which the thermal couple is attached.

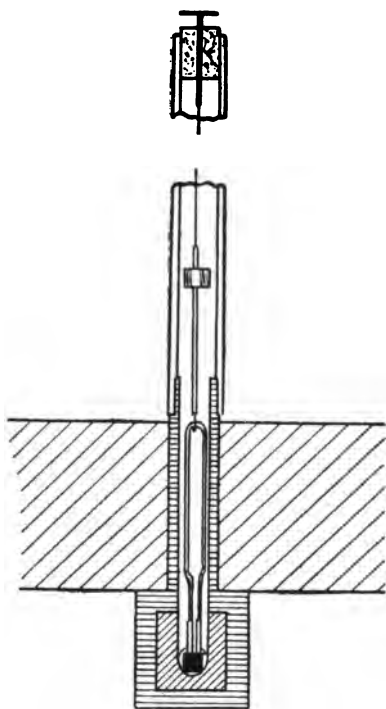


FIG. 100.—BOY'S RADIO-MICROMETER.

The radio-micrometer is one of the most sensitive instruments for the detection of radiant heat, as it may be made of very low thermal capacity, and the quartz-fibre suspension enables the coil to move in response to the feeblest attraction caused by the passing of very minute currents. A rise in temperature on the part of the disc of one millionth of a degree Centigrade causes a visible deflection, and the heat radiated by a burning candle may be detected at a distance greater than two miles. The chief drawback of the radio-micrometer in practical use is its lack of portability, as, like all delicately suspended galvanometers, it must be fixed in position to take observations,

whereas a thermopile or the grating of a bolometer may be moved to any desired spot to receive radiations.

Nichol's Suspended-Vane Radiometer.—The latest and most sensitive heat-detector is a modification of the radiometer of Crookes, which, as shown in Fig. 101, consists of a number of arms radiating from a central support in an exhausted globe. At the end of each arm is placed a mica vane, blackened on one side. Radiant energy, on striking the vanes, is absorbed to a greater extent by the blackened sides of the vanes than by the unblackened, and a repulsive motion of the vanes away from the source ensues, owing to the gaseous molecules in the tube being repelled from the hot side of the vanes. The

action resembles that of a lawn sprinkler, which revolves in the opposite direction to that at which the water shoots out. In Nichol's instrument the central arm, instead of being pivoted, is suspended by a quartz fibre to which a mirror is attached, from which a spot of light is reflected on to a scale. When a star of the first magnitude is focused on to one of the vanes by means of a concave mirror, a distinct movement of the spot of light along the scale is noted. A bolometer or radio-micrometer is not capable of detecting the radiant energy received from a star.

Experiments on the Radiating Power of Surfaces.—By the aid of a thermopile and astatic galvanometer Melloni investigated the relative quantities of heat radiated from different surfaces at different temperatures, and also the quantities absorbed. Four sources of heat were employed, as follows:—

1. A copper cube containing boiling water, the surfaces of which were coated with the substance investigated.

2. A copper-plate, heated by a spirit-lamp to about 400°C ., which could similarly be coated.

3. A spiral of platinum wire, raised to incandescence in the flame of a spirit-lamp. Radiations from this were received on different surfaces, in order to compare the absorptive powers.

4. A Locatelli oil-lamp, the flame of which was kept constant by an arrangement for maintaining the level of the oil.

In expressing the results, the radiating and absorbing power of lamp-black were taken as 100, and the values for other substances referred to this figure. Lamp-black, however, is not a perfect radiator, and consequently the figures must be regarded as comparative, and not expressing true percentages of energy radiated or absorbed. The following table shows the results obtained at 100°C .

RELATIVE RADIATING POWERS AT 100°C .

Lamp-black	100	Platinum	17
White lead	100	Polished brass	7
Glass	90	„ copper	7
Indian ink	85	„ gold	3
Steel	17	„ silver	3

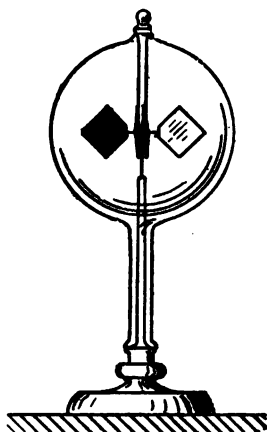


FIG. 101.—CROOKES' RADIOMETER.

The above figures were obtained by receiving the radiations from the sides of a cube containing boiling water directly on the thermopile, one face of the cube being removable in order that plates with different surfaces might be inserted. In determining absorptive powers the radiations from various sources were received on a plate of copper coated with the substance under trial. The other side of this plate was coated with lamp-black, and presented to the thermopile. The heat absorbed caused the temperature of the plate to rise, and consequently the thermopile was affected by radiations from the lamp-black side. The greater the absorptive power, the higher was the temperature of the plate, and hence the greater the effect on the thermopile. The figures obtained for several surfaces are appended.

Substances	Oil Lamp	Incandescent Platinum	Copper at 400° C.	Hot Water, Cube at 100°C.
Lamp-black . . .	100	100	100	100
Indian ink . . .	96	95	87	85
White lead . . .	53	56	89	100
Shellac	48	47	70	72
Metallic surface . .	14	13.5	13	13

The above figures show that for most substances the absorptive power varies with the character of the incident radiations, and the same is true of the emissive power. Luminous waves possess a shorter wave-length than non-luminous waves, and a substance capable of absorbing or emitting the longer waves freely might have little power with respect to the shorter waves. Thus for the non-luminous waves from a substance at 100° C., white lead is equal to lamp-black in absorbing and radiating powers, but only about one-half as good for the radiations from a luminous source. The heat waves received by polished metals are largely reflected by the surface, whether incident upon the surface externally or internally, and hence such surfaces have little absorptive or emissive power.

It may be seen from the above results that nothing is gained by painting a hot-water radiator black, as, at 100° C., white lead or any dull paint is equally good. If varnish or a metallic paint be used, however, the radiating power is considerably diminished. The superiority of a coal or coke fire for warming a room depends upon the high temperature and consequent large quantity of radiant energy, and also upon the black surface of the fuel, which radiates freely.

In both these respects a coal fire is superior to a gas fire, in which, owing to the small radiating power of a flame, balls of firebrick or pieces of asbestos are introduced to radiate the heat. The temperature in the gas fire does not rise so high, on the average, as the coal fire, and the heated materials have a smaller radiating power than coal. Much of the heat of a coal fire may be prevented from escaping up the chimney by making the back of the fireplace of firebrick, bevelled so as to reflect heat into the room. Ultimately the firebrick becomes red-hot, and adds greatly to the radiations received from the fireplace.

Other things being equal, dark-coloured substances in general possess a higher absorbing power for waves from a luminous source than those of a light colour. For this reason white or light-coloured clothing is cooler than dark-coloured in summer, inasmuch as less radiant heat from the sun is absorbed by the former.

Actual Quantity of Energy Radiated by different Surfaces.—The relative radiating powers as found by Melloni's experiments afford no clue to the actual quantity of energy radiated under different conditions. Later investigations by Lummer, Kurlbaum, Pringsheim, and others, have resulted in the determination of the energy constant for black-body and other radiations at different temperatures. In these experiments an enclosure similar to that illustrated in Fig. 97 was employed to determine the quantity of radiant energy for a black body at low temperatures, whilst for higher temperatures a tube heated externally by electricity was employed. For exposed surfaces the substance was heated electrically or otherwise to definite temperatures ascertained by a pyrometer. Taking as a starting-point the Stefan-Boltzmann law—

$$E = K (T_1^4 - T_2^4),$$

the value for the constant K was found by Kurlbaum to be 5.32×10^{-12} , when the energy E is expressed as watts per square centimetre of surface, under black-body conditions. If the energy radiated be expressed as calories per square centimetre per second, the value of K is 1.28×10^{-12} . In the following table the energy radiated in calories per square centimetre per second is given for varying values of T_1 , the temperature of the body receiving the radiations (T_2) being constant at 300° absolute, or 27° C. The values for a black body, oxide of iron, and platinum are given for the purpose of comparison.

The superiority of a black body over other surfaces with respect to energy radiated is plainly indicated in the table (p. 370). It

Absolute Temperature of Hot Body (T_1)	Absolute Temperature of Body receiving Radiations (T_2)	Calories per Square Centimetre per second from		
		Black Body	Oxide of Iron	Platinum
1200	300	2.65	1.23	0.33
1100	"	1.87	0.79	0.21
1000	"	1.27	0.50	0.128
900	"	0.83	0.32	0.075
800	"	0.52	0.175	0.039
700	"	0.30	0.105	0.019
600	"	0.155	0.047	0.007
500	"	0.070	0.021	0.0015
400	"	0.022

will be noted, however, that this superiority becomes less marked as the temperature rises; thus at 500° abs. the relative quantities radiated by a black body and oxide of iron are as 3.32 to 1, whereas at 1200 the ratio is 2.16 to 1. A similar improvement in radiating power at higher temperatures is noticeable in the case of platinum also; and it may be stated, in general, that the higher the temperature the nearer the radiations approximate to those of a black body.

It will be seen that the radiations from an oxide of iron surface at 1200° abs. are slightly less than those obtained from a black body at 1000° abs. Hence a block of iron or steel, coated with oxide, which when under black-body conditions in a furnace shows a temperature of 1200° abs. or 927° C. on a heat radiation pyrometer, will only indicate 1000° abs. or 727° C. when sighted outside the furnace. It should be remembered that the figures given apply only to total energy radiated, and that the relative luminosities of a black body and a hot surface do not show the same proportion. A block of iron or steel, when sighted inside and outside the furnace with an optical pyrometer, will show a less apparent difference in temperature than is noticed with a Féry heat-radiation pyrometer, which measures the total energy as distinct from the intensity of luminous rays.

The radiations from a lamp-black surface, at temperatures below 600° abs., approximate closely to those of a black body.

Scattering, or Diffusion of Radiant Heat.—When radiant heat falls on a powder, a portion is absorbed, whilst the remainder is reflected in an irregular manner from granule to granule of the powder, ultimately escaping into the surrounding air in all directions.

This effect is specially noticeable with white powders, and resembles the scattering of light produced by the same means. To this action is due the great heat experienced in the vicinity of a white wall upon which the sun is shining. It is customary to whitewash the glass roof of a workshop in summer, as by doing so the heat rays from the sun are largely scattered, and prevented from passing through the glass. The workshop is thus kept cool without entirely shutting out the light.

Distribution of Energy in the Spectrum.—The energy received from a luminous source consists of a mixture of ether waves of different wave-lengths, which may be separated by means of a prism or diffraction grating. The visible portion of the spectrum consists of waves which are capable of exciting the optic nerve, and so giving rise to the sensation of light. The violet rays, which are bent the most by a prism, have a shorter wave-length than the red rays, which are bent least; whilst intermediate portions have intermediate wave-lengths. Beyond the visible spectrum, however, the existence of ether vibrations may be proved by various means. Thus beyond the violet end the waves are capable of exerting a chemical action on silver salts, and darken a photographic plate exposed in this region. Beyond the red end of the spectrum, waves of greater wave-length may be detected by means of a thermopile or other sensitive detector of radiant heat. The visible spectrum only constitutes a small portion of the total wave-lengths that may be traced by suitable detectors.

When the waves existing in any portion of the spectrum—whether visible or invisible—are absorbed by the blackened surface of a thermopile or bolometer, the energy received is converted into heat; and consequently the indications of these instruments afford a clue to the quantity of energy corresponding to different wave-lengths. Hence, if the heat-detector be placed successively in different parts of the spectrum, the distribution of energy in the various regions may be determined, as all the types of energy existing in different portions are converted into an equivalent quantity of heat when absorbed by the blackened surface of the instrument. Tyndall, who investigated the spectrum of an arc-lamp with a thermopile, obtained the results shown in graphic form in Fig. 102. No energy was detected beyond the violet end of the spectrum, but as the thermopile was moved towards the red end an increasing effect was obtained. Beyond the visible red a rapid increase in the energy received by the thermopile was noted, which attained a maximum and afterwards diminished as the instrument was moved further from the visible red.

The later investigations of Langley and others confirm, in general, the results obtained by Tyndall. The sensitive indications of the

bolometer, as used by Langley, enabled the existence of radiant energy to be traced in portions of the spectrum where the quantity was too small to affect a thermopile. By the aid of this delicate instrument the distribution of energy in all parts of the spectrum was accurately measured, and the results obtained with spectra obtained from different sources were recorded. These investigations led to an important generalisation, which will now be considered.

Wien's Laws.—It was noticed by Langley and others that as the temperature of the luminous source increases, the position in the spectrum at which the maximum energy occurs moves towards the visible region. This is indicated in Fig. 103, in which it will be seen that the distribution curve for a spectrum from a source at 2000° attains its maximum at some distance in the region beyond the red.

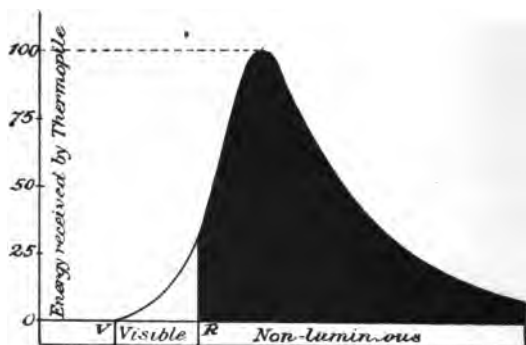


FIG. 102.—TYNDALL'S CURVE OF ENERGY DISTRIBUTION IN THE SPECTRUM OF AN ARC LAMP.

At 3000° the maximum occurs nearer the red, but still in the invisible portion; at 4000° the maximum is just in the visible part; whilst at 5000° and 6000° the maximum position has shifted still further into the visible region. Hence, as the temperature rises, the wave-length corresponding to the position of maximum energy diminishes.

The connection between temperature and wave-length is expressed by the following law, arrived at by Wien from theoretical considerations: "As the temperature increases, each wave-length in the spectrum diminishes in such a manner that the product of wave-length and absolute temperature is constant." Or, expressed in symbols,

$$\lambda T = \text{a constant,}$$

where λ = wave-length, and T the absolute temperature. As this law applies to each wave-length in the spectrum, the special wave-

length corresponding to the position of maximum energy is also governed by it, and hence

$$\lambda_{\max.} T = \text{a constant.}$$

When the source is a black body, and the wave-lengths are measured in millionths of a centimetre, the value of the constant is 294,000.

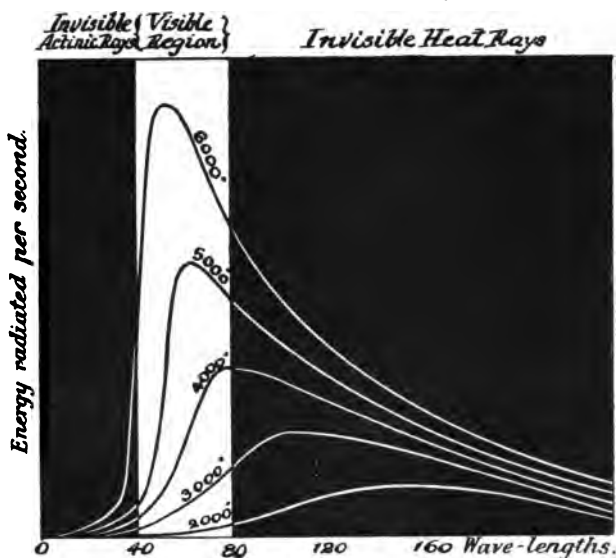


FIG. 103.—ENERGY CURVES FOR SPECTRA OBTAINED FROM SOURCES AT DIFFERENT TEMPERATURES.

Hence, by dividing 294,000 by the absolute temperature of the source, the wave-length of maximum energy is obtained. The figures for several temperatures are tabulated below :—

Absolute Temperature	Wave-Length of Maximum Energy
1000	294
2000	147
3000	98
4000	73
5000	59
6000	49

For radiations from other sources than a black body, the law still holds true, although the value of the constant is different. For polished platinum the constant is 262,600.

By combining the above law with the Stefan-Boltzmann law, Wien obtained the following relation for a black body :—

$$E_{\max.} T^{-5} = \text{a constant,}$$

where E is the energy corresponding to the wave-length of maximum energy, and T the absolute temperature. Both this and the previous laws have been fully verified by the experiments of Lummer, Pringsheim, and others. The second law may be expressed as follows: The energy corresponding to the wave-length of the maximum energy varies directly as the fifth power of the absolute temperature of the source. When E is expressed in ergs per second, the value of the constant is 2188×10^{-17} , or

$$E (\text{max.}) = 2188 \times 10^{-17} \times T^5.$$

Hence, at 1000° abs., $E (\text{max.})$ will equal 21.88 , the wave-length corresponding to E , from the first law, being 294 micro-centimetres.

Effect of Temperature on Luminosity.—It will be seen from the foregoing that a rise in temperature results in the shifting of the position of maximum energy towards the visible part of the spectrum. The result is that a greater proportion of the total energy appears as light at higher temperatures, and if the photometric intensity of the light received from a given body at different temperatures be measured, the relation

$$\frac{I_1}{I_2} = \left(\frac{T_1}{T_2} \right)^\alpha$$

is found to hold good, where I_1 and I_2 are the intensities corresponding to absolute temperatures T_1 and T_2 . The value of α varies considerably, being 30 when T_1 is 800° and T_2 900° , but only 12 when the absolute temperatures are 2000 and 2100. The value of the exponent α is approximately equal to $\frac{25000}{T}$ at a given absolute temperature T .

The great increase in luminosity observed in an incandescent electric lamp, as the temperature rises owing to an increase of voltage at the terminals, will be readily understood from the above relation. The first visible red corresponds to a temperature of 800° abs., and, on raising the temperature to 900° abs., the luminosity increases in

the ratio $\left(\frac{900}{800}\right)^{80}$, or 34.1. At higher temperatures the rate of increase is less than this, but even at 2000° the value of α is 12. The limit of economic burning of a carbon filament lamp is reached at 2000° abs., any further increase in temperature resulting in a rapid blackening of the interior of the lamp, due to vaporisation of the carbon, which largely prevents the light from passing to the exterior. On the contrary, tantalum and tungsten filaments can be used with safety at 2100° or 2200° absolute, with a great gain in luminosity. Taking the former figure for comparison with a carbon filament at 2000°, the relative intensities are expressed by the ratio $\left(\frac{2100}{2000}\right)^{12} = 1.8$; and with the temperature at 2200 the ratio is $\left(\frac{2200}{2000}\right)^{12} = 3.1$. It is evident, therefore, that for a given candle-power much less energy will be required by the metallic filament lamp at the higher temperature, as the extra energy required to produce the higher temperature bears a much smaller proportion to the total energy than the proportionate gain in luminosity. Thus, if the loss of energy from the lamp be due to radiation only, the ratio of energy received at 2200° and 2000°—which is equal to the energy radiated—would be practically $\left(\frac{2200}{2000}\right)^4 = 1.46$, according to the Stefan-Boltzmann law; whereas the luminosity is 3.1 times as great.

Example.—A lamp giving 32 c.p. at 100 volts and 1.28 amperes, at a temperature of 2000° C., would give $(32 \times 3.1) =$ approximately 100 c.p. at 2200° C. The energy requisite to run the lamp at the higher temperature would be (roughly) 1.5 times as great; hence if 100 volts were maintained at the terminals the current required would be 1.92 amperes. The relative cost per c.p. would be $\frac{100}{32} \times \frac{1.28}{1.92} = 2.1$ nearly; that is, the cost of the light at the lower temperature would be more than twice as great as when the lamp is run at the higher temperature.

At the present time, the extra cost of metal filament lamps must be placed against the saving effected in current; but in spite of this it would appear that the carbon filament lamp will be superseded by the former class.

Diathermancy, or Heat Transparency.—As heat waves are identical with light waves, it might be expected that certain substances permit heat waves to pass through them, just as glass, quartz, etc., are transparent to light. This is found to be the case, although the proportion

of the incident heat transmitted through a medium may be different to the proportion of light which passes through. The relative heat-transmitting powers of substances can be determined by interposing a layer between a source of heat and a thermopile, when the diminished deflection of the galvanometer indicates the amount shut off by the substance under trial. The radiant heat absorbed by air is extremely small, and may be neglected in the experiment.

Tested in this manner, it is found that rock-salt is more transparent to heat waves than any other substance, and this superiority holds, whether the source of heat be luminous or non-luminous. Other substances, whilst permitting the passage of the heat from a luminous body freely, are practically opaque to radiations of longer wave-length such as are received from a non-luminous source. In the following table the percentage of heat transmitted by various materials from four different sources is given :—

Thickness = 2.6 mm. Substance	Source of Heat			
	Flame of Oil Lamp	White-hot Platinum	Blackened Copper at 300° C.	Blackened Copper at 100° C.
Rock-salt . .	92	92	92	92
Fluorspar . .	78	69	42	33
Mirror glass . .	39	24	6	0
Alum . . .	9	2	0	0
Ice	6	0	0	0
Argand Burner				
Solution of Alum .	12
„ Salt .	12
Distilled water .	11
Carbon disulphide .	63

The foregoing table shows that different substances are more permeable to certain wave-lengths than to others, which is also true with respect to light. Glass transmits luminous waves of shorter wave-length with comparative freedom, but is almost entirely opaque to the non-luminous waves, which have a greater wave length. Hence, in a greenhouse the luminous waves from the sun enter freely through the glass, but, being absorbed by the various objects, the energy is expended in producing a rise of temperature, and the radiations from the objects are then of the non-luminous type, which cannot escape

through the glass. In consequence of this the temperature rises, the glass building acting as a trap for the heat received from the sun.

A body which transmits light freely may be almost opaque to heat, and *vice versa*. Alum, ice and water, for example, are transparent to light, but do not readily transmit heat waves. On the other hand, a solution of iodine in carbon disulphide is practically opaque to light but extremely permeable to radiant heat. All the radiant heat absorbed is expended in raising the temperature of the absorbing substance.

Gases, in general, permit of the passage of radiant heat with great freedom, the proportion absorbed being very small. Hence the sun's rays pass through the atmosphere without causing a sensible rise in temperature, but are absorbed by the surface of the earth. The atmosphere is heated by contact with the warm surface, and the rise in temperature is noted as far as the convection currents rising from the surface reach. For this reason, even on a hot day, the temperature a few thousand feet above the earth's surface may be below freezing-point, as may be discovered by ascending in a balloon.

Vapours, in distinction to gases, absorb a notable quantity of the total radiant heat received. Water vapour in the atmosphere thus exercises an effect in partially stopping the radiant heat received from the sun during the day, and in preventing the escape of radiant heat from the surface at night. Condensed water-vapour in the form of clouds, like ordinary water, is practically opaque to non-luminous radiations, and hence on a cloudy night the surface of the earth is seldom cooled sufficiently by radiation to permit of the formation of dew or hoar-frost.

Selective Emission and Absorption.—It is noticed, in general, that a substance absorbs almost entirely the rays it emits itself when heated, and in consequence is practically opaque to such rays. Thus rock-salt, although transparent to heat waves from most sources, is largely opaque to the radiations received from another piece of rock-salt. This is explained by assuming that radiant heat is emitted when the molecules of a body are in a state of vibration, which vibration is communicated to the ether in the form of waves; and when these waves impinge on identical molecules to those producing the ether waves, the energy is expended in setting the molecules of the receiving substance into vibration; as, being identical, the molecules will respond to such waves sympathetically. If the receiving body differ from the radiating substance a partial response only will be obtained, and some of the waves will be transmitted.

In this manner is explained the fact that glass, when heated, gives

out a large proportion of non-luminous heat, and little light ; for the vibrations of the molecules of glass are such as to respond to and absorb non-luminous radiations, and hence, when agitated by heat, the molecules will generate the same kind of waves—that is, non-luminous. Viewed from this stand-point, the meaning of the fact that alum, for example, transmits 9 per cent. of the radiations of an oil-lamp, is that the molecules of alum respond to waves which convey 91 per cent. of the total energy, but not to the waves which represent the remaining 9 per cent.

CHAPTER XX.

THE CONVERSION OF HEAT INTO WORK. LAWS OF
THERMODYNAMICS.

First Law of Thermodynamics.—This law may be expressed as follows: "Heat and work are mutually convertible; a given quantity of heat being capable of performing a fixed amount of work, and conversely, a given amount of work is capable of producing a fixed quantity of heat." As the result of the work of many investigators, foremost of whom must be placed Dr. Joule, of Manchester, this law has been established on a secure experimental basis, and is the fundamental principle governing the action of all heat engines. One important conclusion derived from this law is that a limit exists to the amount of work obtainable from the consumption of a given weight of fuel, and when the work represented by 1 unit of heat—termed the "mechanical equivalent"—is known, the limit of the work that may be derived from 1 lb. of fuel may be obtained numerically, and used to form a standard to which the actual performance of an engine may be compared. A brief description will now be given of the methods by which this important numerical relation has been obtained.

Joule's Experiments.—The earliest form of apparatus used by Dr. Joule consisted of a vessel, containing water, in which paddles were caused to rotate by means of falling weights. The friction between the paddles and the water gave rise to heat, the quantity produced being determined by noting the rise in temperature, and knowing the weight of water used and the water equivalent of the vessel and paddles. The work done in producing this quantity of heat was obtained by multiplying the weights by the distance fallen. Allowance was made for radiation of heat by the vessel, and for the friction of the pulleys and other attachments by means of which the falling weights actuated the paddles. By equating the heat produced to the work done, the work equivalent of one heat unit was determined. In later experiments Joule employed iron paddles rotating in mercury, and also cast-iron rings rubbing against each other under mercury.

As a result of these experiments, Joule adopted 772 foot-pounds as the work equivalent of one British thermal unit.

In still later experiments the paddles were caused to rotate continuously, and the vessel supported on a hydraulic bearing. The friction between the moving liquid and the sides of the vessel tended to make the latter rotate. A cord was wound round a groove in the side of the vessel, and passed over pulleys to pans in which weights were placed. The rotation of the paddles was conducted at such a rate as to maintain the weights suspended in a fixed position, and the number of revolutions was recorded by a counter. The heat produced was measured as before; the work done was equal to that which would have been done had the weights been allowed to fall, and, by their falling, to rotate the calorimeter through the observed number of revolutions, that is, $\pi d n w$, d being the diameter of the vessel, n the number of revolutions, and w the sum of the suspended weights. This apparatus gave 772.55 foot-pounds as the equivalent of a British thermal unit.

Hirn's Experiments.—Instead of converting work into heat by friction, Hirn employed percussion. A large block of stone, faced with iron, was suspended by cords, and served as an anvil; whilst a similarly suspended piece of steel served as a hammer. A piece of lead was placed between the two, and the hammer raised and allowed to fall so as to drive the lead on to the anvil. The work done was measured from the known weight of the hammer and the distance it had fallen, due allowance being made for recoil of the anvil, etc. The heat produced was determined by noting the rise in temperature of the known weight of lead, and equated to the work done. The figure obtained, in the units adopted above, was approximately 768.

In further experiments Hirn compared the heat which disappeared in the cylinder of a steam engine with the output of work as obtained from the indicator diagram. After making due allowance for radiation and other losses, Hirn obtained results ranging between 750 and 762. Considering the difficulties attendant in obtaining accurate results by this method, the figures afford a striking confirmation of the existence of a constant relation between heat and work, no matter how the one may be converted into the other.

Rowland's Experiments.—The apparatus used by Professor Rowland, of Baltimore, was the same in principle as that of Joule. By using a more efficient form of paddle, and employing an engine to secure a rapid rotation, Rowland was able to obtain a rise in temperature of 40° C. per hour, or even more, whereas the rate in Joule's apparatus was only at the rate of .62° C. per hour. Any

small error in the reading of the thermometer, therefore, influenced the result to a much less extent in the former case than in the latter; thus an error of $\frac{1}{1000}^{\circ}$ C. on a rise of 10° only causes an error of 1 in 1000; whereas on a rise of $\cdot 62$ the error would be 1 in 62. Moreover, the mercury thermometers used by Joule had not been compared with the gas scale, which is now adopted as the standard of temperature.

Rowland used an accurate dynamometer to measure the work done by the engine in driving the paddles, and on equating this to the work done, obtained the figure 778 ft.-lb. as the equivalent of 1 British thermal unit.

Determinations by Electrical Methods.—The units employed in electrical measurements are based upon the C.G.S. system, and, assuming that such units are in strict accordance with the values intended to be assigned to them, it is possible to determine the mechanical equivalent of heat by electrical means. When a current of electricity is passed through a resistance, heat is produced, and if the work equivalent of the electricity expended be obtained by calculation, it may be equated to the heat generated, and the work equivalent of one heat unit deduced. From the manner in which the units of electricity have been chosen, a current of 1 ampere, maintained by a difference of potential of 1 volt between the ends of a resistance (which would therefore be equal to 1 ohm) does work at the rate of 10,000,000 (ten million) ergs per second; that is, 1 watt represents work at the rate of 10,000,000 ergs per second. Hence, if a known current of electricity be passed through a wire for a given time, the work represented will be the product

$$(\text{volts} \times \text{amperes} \times \text{time in seconds} \times 10,000,000) \text{ ergs.}$$

As all the electrical energy is converted into heat, the work equivalent in ergs of the heat produced may be equated to the above, from which

$$J H = (C V t \times 10,000,000) \text{ ergs,}$$

where J = the mechanical equivalent of 1 heat unit, and H the number of heat units produced. By measuring the current passing, the voltage between the terminals of the resistance, and the heat produced, the value of J may be calculated from this equation. To perform the experiment, a wire resistance may be placed in a suitable calorimeter, and a current passed through it for a known time. By noting the rise in temperature, and accurately measuring the current

and voltage at the terminals of the resistance, the necessary data may be obtained.

Determinations on the foregoing lines have been made by Griffiths, Callendar, and others, with the result that the figure obtained by Rowland—778—has been confirmed. It may therefore be assumed that this figure is a close approximation to the true value.

Value of "J" in Terms of Different Units.—The constant character of the relation between heat and work having thus been established, the first law of thermodynamics may be expressed symbolically as

$$W = J H,$$

where W = work done in producing a quantity of heat H , and J = the mechanical equivalent of 1 heat unit. If H represent 1 British thermal unit, $W = 778$ ft.-lb. = J . If the heat unit chosen be 1 lb. of water raised 1° C., the corresponding value of J will be $778 \times \frac{9}{5} = 1400$ ft.-lb. If the work be expressed in centimetre-grams, and $H = 1$ calorie, $J = 1400 \times 30.54 = 42,750$ cm.-grams, = 42,000,000 ergs (approx.). Tabulating these values,

778 foot-pounds	=	1 B.Th.U.
1400 "	=	1 lb.-° C. unit
42,750 centimetre-grams	=	1 calorie
42,000,000 ergs	=	1 calorie

The equivalent of 1 calorie in foot-pounds is

$$\frac{1400}{453.6} = 3.09 \text{ ft.-lb.}$$

Efficiency of an Engine.—The efficiency of an engine is defined as the ratio of the work done by the engine to the energy provided. As heat may be expressed in work units, the ratio may be written

$$\text{Efficiency} = \frac{\text{work done by engine}}{\text{work equivalent of heat provided}}.$$

It is customary to multiply this ratio by 100, the efficiency then being expressed as a percentage. A few examples, illustrating the use of the mechanical equivalent of heat in calculating efficiencies, etc., will now be given.

Example 1.—If all the heat obtained by burning 1 lb. of coal, of calorific value 14,000 B.Th.U. per lb., could be converted into work ($14,000 \times 778$) = 10,892,000 ft.-lb. would result. For many reasons it is only possible, in the very best engines, to convert a

comparatively small portion of the heat of the coal into work; the above figure, however, represents the actual energy stored in 1 lb. of the coal.

Example 2.—An engine works at the rate of 10 horse-power, and consumes 24 lb. of coal, of calorific value 7500 calories per gram, in one hour. To find the efficiency of the engine.

$$\text{Efficiency} = \frac{\text{work done}}{\text{work equivalent of heat provided}}$$

$$= \frac{10 \times 33,000 \times 60}{24 \times 7,500 \times 1400} = .0785$$

or 7.85 per cent.

(Note that if 1 gram of coal raises 1 gram of water 1°C. in temperature, then 1 lb. of coal raises 1 lb. of water 1°C. in temperature.)

Example 3.—A steam engine of 15,000 horse-power, working with an efficiency of 10 per cent., and using coal of calorific value 8000 calories per gram (or lb.-°C. units per lb.), will consume 26,518 lb. or nearly 11 tons per hour, since

$$.1 x = \frac{15,000 \times 33,000 \times 60}{8000 \times 1400}$$

where x = lb. of coal burnt per hour.

In the practical determination of the efficiency of an engine, the work done may be obtained from an indicator diagram, and expressed as indicated horse-power (I.H.P.); or may be measured by a brake-test on the engine, and stated as brake horse-power (B.H.P.). The work rate as recorded by an indicator diagram does not take into account frictional and other losses in the engine and its connections, and consequently the efficiency deduced by this means has a value higher than that calculated from the results of a brake-test, which measures the work available for external purposes. In obtaining the work equivalent of the heat provided, it is necessary to know the quantity and calorific value of the fuel used. In a steam-engine plant some of the heat of the fuel escapes up the chimney, and by radiation from the boiler surfaces, so that all the heat of combustion does not enter the cylinder. If the efficiency of a steam-engine plant, however, is to be compared to that of an internal combustion engine, the furnace and boiler losses must be regarded as inseparable from the steam engine; and a fair comparison would not be obtained if only the heat entering the cylinder were con-

sidered. The practical efficiency of any heat engine is therefore expressed by the ratio

$$\frac{\text{work available for external purposes}}{\text{work equivalent of heat furnished by the fuel used}}.$$

The theoretical efficiency of any heat engine will be shown later to depend upon the absolute temperatures at which heat is received and rejected. In this case a total absence of loss by radiation, friction of parts, or from any other cause, is assumed.

The Second Law of Thermodynamics.—This law, as stated by Clausius, is as follows: "It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature; or heat cannot of itself (that is, without compensation) pass from a colder to a warmer body."

Lord Kelvin's statement of the same law is, that "It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of surrounding objects."

This law, as expressed by either of the foregoing statements, applies only to cases in which the "body" or "portion of matter" is taken through a complete cycle of operations, so as to end in the same thermal condition as that which it possessed at the beginning. Thus by passing steam at 100°C. into a strong solution of calcium chloride, a higher temperature than 100°C. is reached, heat passing from the colder steam into the hotter solution; but this is a single operation, and the steam does not end as it began. In like manner a compressed gas may do work on expansion, and, by expanding, cool itself below the temperature of surrounding objects; here again, however, the process is not cyclic, and the gas is left in a different thermal condition to that originally possessed. Broadly stated, the second law of thermodynamics expresses the fact that in all engines in which heat is converted into work, the process consists in extracting heat from a hot substance, some of which is converted into work, whilst the remainder is imparted to a colder substance. In no case can the converse process be performed, namely, to extract heat from the colder substance, a portion of which would become work and the residue go to the hot body. The law is thus founded upon universal experience. In a steam engine the hot steam enters the cylinder and gives up a part of its heat in driving the engine, and the remainder to the condenser; and by no possible device could the engine be made to give out work by taking in the colder steam from the condenser, using some of the heat possessed to

drive the engine and giving up the remainder to steam at a higher temperature.

It should be remembered, however, that it is possible, by providing work from an outside agency, to extract heat from the cold part of an engine and to impart a portion of the heat extracted to the warm part. This is what occurs in a refrigerating machine; but, instead of deriving any mechanical effect from the cycle of operations, it is necessary to supply energy from without to make the process possible. For an engine to work in a manner contrary to the second law of thermodynamics, it would be necessary to construct a refrigerating machine capable of working not only without external aid, but in such a manner as continuously to perform external work—which is contrary to all experience. The truth of the law, and of deductions made from it, may, therefore, be regarded as firmly established.

The efficiency of an ideal heat engine will now be considered from the standpoint of the two fundamental laws of thermodynamics.

Carnot's Ideal Engine.—The conditions governing the action of heat engines in general were first brought to notice by Sadi Carnot in 1824. In his famous essay on "The Motive Power of Heat," Carnot introduced the conception of cycles of operation, and also the principle of reversibility; and thus laid the foundation of our modern knowledge concerning the conversion of heat into work in any type of engine. The ideal set of operations described by Carnot cannot be realised in practice; but, just as in other connections a "perfect" gas and a "frictionless" surface serve as useful standards of comparison, so an ideal set of operations are of service in judging the actual performance of an engine. Moreover, a set of operations in which the maximum efficiency would be realised serve as a guide to follow, as far as practicable, in the design of an engine, and a study of these operations is therefore of the greatest utility.

The action of Carnot's engine may be understood by reference to Fig. 104. A cylinder, supposed to possess non-conducting sides and a perfectly-conducting end, is fitted with a non-conducting piston, and contains the working substance. A hot body and a cold body, each kept at a constant temperature, and a non-conducting stand, are also assumed to be available; and the operations performed are as follows:—

1. Starting with the working substance at the temperature (T_1) of the hot body, and the end of the piston in the position $a-a$, the cylinder is placed on the non-conducting stand, and the piston liberated, allowing the working substance to expand and drive a machine connected with the engine. In performing this work, the medium

2 C

parts with heat energy, and its temperature falls. This process is allowed to continue until the temperature of the cold body (T_2) has been reached, when the piston is at $b-b$.

2. The cylinder is now placed on the cold body, and the piston forced down to a position $c-c$. External work is requisite to con-

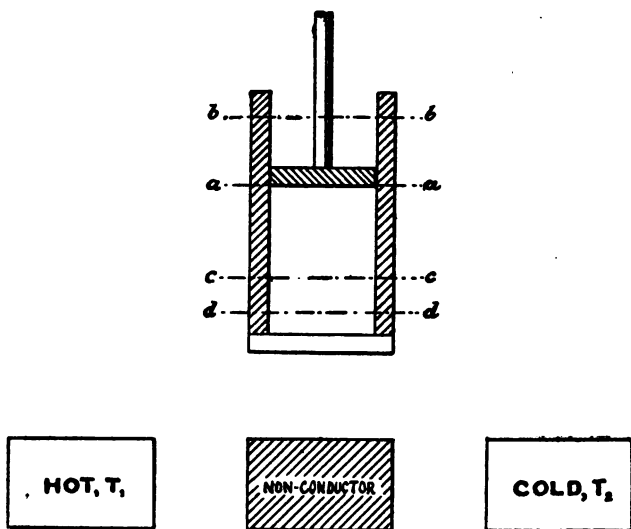


FIG. 104.—CARNOT'S IDEAL ENGINE.

duct this process, and is converted into heat; but, as the end of the cylinder conducts perfectly, all the heat thus produced passes into the cold body, and hence the temperature of the medium remains at T_2 .

3. The cylinder is again transferred to the insulating stand, and the piston further depressed. External work is again necessary, but the heat produced remains in the medium. This process is continued until the temperature rises to that of the hot body (T_1), the piston reaching a position $d-d$.

4. The cylinder is placed on the hot body, and the medium allowed to expand, doing work. The temperature is prevented from falling, owing to heat continuously passing into the cylinder from the hot body. This operation is allowed to go on until the piston arrives at the original position $a-a$. The medium is now in the same condition as at the commencement, the temperature being T_1 and the volume identical with the starting volume.

These four operations constitute a cycle which may be repeated

indefinitely. Moreover, as the working substance or medium is in exactly the same condition at the end of the cycle as at the commencement, it follows that the net output of work is not derived from the energy stored up in the medium, but from the heat furnished by the hot body. Consequently, the work done by an engine working with this cycle is independent of the medium used, which may be a gas such as air or hydrogen, or vapour such as steam or ether vapour. The working substance is only the instrument by means of which heat is converted into work; and although its condition is altered during the several operations, the original state is regained at the end of the cycle. An analogy is furnished by the spring of a watch or clock, which acts as a medium for converting the energy expended in winding it into the work necessary to actuate the mechanism, finally returning to its original condition. The work done does not depend upon whether the spring is made of steel or phosphor-bronze, but only upon the energy expended in winding it.

Before considering further the cycle of operations in Carnot's engine, it may be of advantage to compare the action of a steam engine with the set of operations described. The hot body, or source of heat in the steam engine is the boiler, and the cold body the condenser. The period during which steam enters the cylinder is the counterpart of operation (4) in Carnot's cycle, and the expansive working, after cut-off, corresponds to operation (1). After the exhaust is open, the conditions of operation (2) are partially realised; but here the analogy ends, as it is not practicable to retain the steam in the cylinder and to re-heat it *in situ* to its original temperature.

The study of Carnot's cycle of operations is much facilitated by reference to the indicator diagram that would be obtained from the ideal engine. Assuming, for the sake of simplicity, that the working substance is a perfect gas—although the diagram could be worked out for any medium capable of going through the necessary changes of volume—the starting pressure and volume may be represented by aA and Oa in Fig. 105. The first operation is indicated by the line AB , and as this process consists of an expansion without heat entering from without, the line AB will be an adiabatic (see Chapter VI.). The second operation is a compression at constant temperature, the heat produced by the compression escaping to the cold body; hence the line BC , which represents this compression, is an isothermal. The third operation, shown graphically by CD , is an adiabatic compression, and the final operation, represented by DA , is an isothermal expansion.

It has previously been shown that the work done in compressing

a gas, or by a gas in expanding, is given by the area bounded by the curve representing the pressure and volume changes, the perpendiculars let fall from the extremity of the curve, and the axis of volume (p. 101). In the second and third operations in the cycle, work is done on the engine, the amount of which is represented by the areas

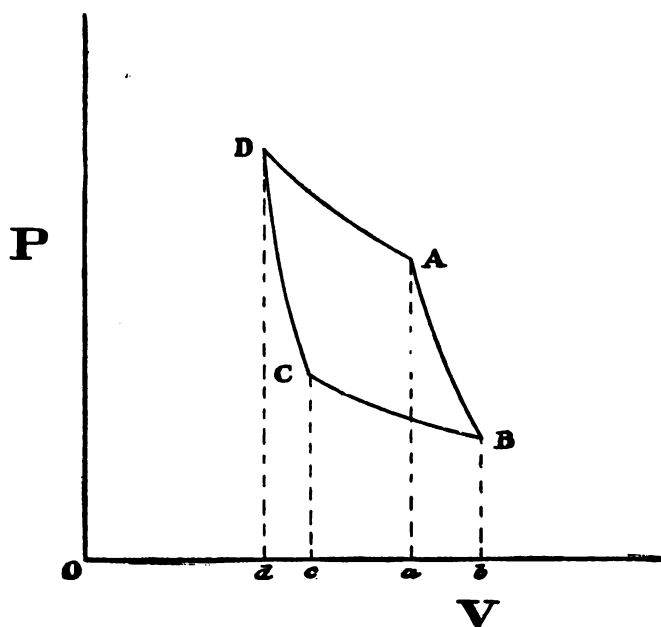


FIG. 105.—GRAPHIC REPRESENTATION OF CARNOT'S CYCLE.

$BCcb$ and $CDdc$ respectively, or taken together the area $DCBbd$. In operations (4) and (1) work is done by the engine, the quantity of which is indicated by the areas $DAad$ and $ABba$, which together equal the area $DABbd$. Hence the net work done by the engine, available for external purposes, is the difference between $DABbd$ and $DCBbd$, that is, the closed figure $ABCD$.

The efficiency of the engine being defined as

$$\frac{\text{work done externally}}{\text{work (or work equivalent of heat) provided}}$$

is represented by the ratio of the areas $ABCD$ and $DABbd$, or

$$\text{efficiency} = \frac{\text{Area } ABCD}{\text{Area } DABbd}$$

But as the working substance does not furnish any of the heat which is converted into work in the cycle, it is evident that the work done is the equivalent of the difference between the amount taken in from the hot body and the quantity rejected, which enters the cold body. Hence, if Q_1 = heat received from hot body, and Q_2 heat entering cold body, the difference $Q_1 - Q_2$ = heat converted into work. Also the total quantity of heat taken in is Q_1 , therefore the efficiency is also expressed by the ratio $\frac{Q_1 - Q_2}{Q_1}$, this expression being the same as that previously obtained, except that it is expressed in heat units instead of work.

Reversibility of Carnot's Engine.—Referring to Fig. 105, it will be noted that the operations of Carnot's engine are represented graphically by two adiabatics and two isothermals; and in following out the processes on the diagram, the closed figure A B C D is traversed in a clockwise direction. It is possible, however, to perform the set of operations in the converse manner, in which case the closed figure would be traversed in a contra-clockwise direction. Starting at the point A, the medium could be compressed isothermally at the higher temperature T_1 , the heat of compression being rejected and driven into the hot body. Arriving at D the medium could be allowed to expand adiabatically, doing external work; and from C to B isothermally, also doing external work, the heat necessary being derived from the cold body at the lower temperature T_2 . Finally the medium could be compressed adiabatically from B to A, and the cycle completed. In this case, however, the work done on the engine in the two compressions is greater than that performed by the engine during the two expansions. It is this surplus work which makes it possible to extract heat from the cold body, and the process is evidently one of mechanical refrigeration.

Comparing the action of a refrigerating machine with a reversed Carnot's engine, the compression of the gas in the cylinder corresponds (approximately) to operation (4) as described above, or from B to A in Fig. 105. When the valve opens to the condenser coils the temperature remains practically steady, any heat generated by further compression being removed by the cooling-water; hence the conditions are isothermal, and may be represented by A D (unless the gas liquefies, in which case A D would be a horizontal straight line). On the return stroke the gas expands adiabatically (approximately), as shown by D C, until, on the evaporator valve opening into the cylinder, an isothermal expansion C B results, the heat necessary being extracted from the refrigerator coils. Hence a refrigerating machine is correctly

described as a reversed heat engine, or as a "heat-pump," which pumps heat from a cold body into a warm one.

The energy ratio of a refrigerating machine has been previously defined (p. 300) as

$$\frac{\text{work equivalent of heat extracted}}{\text{work done in driving the machine}}.$$

In a Carnot engine working backwards, this ratio would be expressed by $\frac{\text{area } DCBbd}{\text{area } ABCD}$, as the work done at the expense of the heat possessed by the medium is represented by the two expansions DC and CB, or, taken together, by the area DCBbd. The compressions BA and AD, conducted by means of external work, are similarly equal to the area BADdb, and the net work expended by (BADdb - DCBbd), or the closed figure ABCD. Or, expressed in heat units, the energy ratio of the machine is equal to $\frac{Q_2}{Q_1 - Q_2}$, in

which Q_2 = quantity of heat extracted from the cold body, and Q_1 the heat equivalent of the work provided during the two compressions.

Reversibility as a Condition of Maximum Efficiency.—No engine can possess a greater efficiency than one which works on a reversible cycle. The condition of reversibility is that all the operations may be conducted in reverse manner by providing the engine with an amount of work equal to that performed by the engine when working directly. This condition is evidently fulfilled by Carnot's engine.

The proof of this proposition is based on the second law of thermodynamics, and is as follows. Imagine an engine B to be more efficient than a reversible engine A. This means that, of a given quantity of heat received, B would convert a larger portion into work than A. If it be so arranged that B drive A backwards, B will be taking heat from the hot body and rejecting it to the cold body, whilst A will act in the converse manner. If the size of the engine B be regulated so that it takes in from the hot body the same quantity of heat as A gives up, no heat will, on the whole, be obtained from the hot body. But if B be more efficient than A it will convert a greater portion of the heat it takes in into work, and will therefore return to the cold body less heat than A takes from it. The compound engine formed by the two, would therefore be capable of doing outside work although heat only enters the system from the cold body—which directly violates the second law of thermodynamics. Hence B cannot be more efficient than A, and also the efficiency of all reversible engines, working under the same conditions, is the same.

Another method of expressing this proof is as under. Let the engine A be made to pass through a refrigerating cycle by B, and let the heat given out by A during the cycle act as the motive power of B. Since A is reversible, the work done in driving it backwards is equal to its output when working forwards, and the heat given out when working as a refrigerator would, if taken in when working forwards, secure an output of work equal to the intake when working backwards. But this same amount of heat is taken in by B, which is assumed to be capable of converting a greater portion of it into heat than A. Hence B would give up less heat to the cold part than A extracts from it, and would be driving A with a quantity of work to spare, due to its superior utilisation of the heat. The combination would, therefore, be acting as a heat engine and refrigerating machine at the same time; or, in other words, producing work continuously by utilising heat from the coldest part. This, as previously shown, is contrary to all experience.

Efficiency of a Reversible Engine in Relation to Temperatures.—

Since the efficiency of a reversible engine is independent of the medium, and the work done is the mechanical equivalent of the difference between the quantity Q_1 taken in at the higher temperature, and the quantity Q_2 rejected at the lower, it follows that the ratio $\frac{Q_1}{Q_2}$ depends upon the temperatures of the hot and cold bodies.

This does not mean that $\frac{Q_1}{Q_2}$ depends upon the temperatures as expressed by the mercury or platinum scales, or upon any scale dependent on the physical properties of matter. Temperature in this connection would be defined as follows: "If an engine, working on a reversible cycle, take in a quantity of heat Q_1 at a temperature T_1 , and reject a quantity Q_2 at a temperature T_2 , the ratio of the temperatures shall be equal to the ratio of the quantities, or $\frac{T_1}{T_2} = \frac{Q_1}{Q_2}$." This is the basis of the thermodynamic scale proposed by Lord Kelvin, and a temperature scale thus founded is independent of any property of matter.

The zero of such a scale would be reached when the quantity Q_2 , rejected at the lower temperature, is nil, since in this case $\frac{Q_1}{Q_2} = \frac{Q_1}{0} = \infty = \frac{T_1}{T_2}$, whence $T_2 = 0$. This leads to the conception of an absolute zero as determined by a substance being entirely void of heat. Further the efficiency under these circumstances would be unity or 100 per cent. since efficiency $= \frac{Q_1 - Q_2}{Q_1} = \frac{Q_1 - 0}{Q_1} = 1$

Hence to secure an engine of efficiency 100 per cent. it would be necessary to have a cold body or condenser kept absolutely void of heat, or at the absolute zero thus defined.

The choice of degrees on this scale is optional. If it be decided to take the melting-point of ice and steam at 760 mm. pressure as standards, then a reversible engine taking in a quantity of heat Q_1 from the steam, and rejecting Q_2 to the ice, would by these quantities determine the ratio of the absolute temperatures of steam and ice on this scale. Or,

$$\frac{Q_1}{Q_2} = \frac{\text{absolute (thermodynamic) temperature of steam}}{\text{absolute (thermodynamic) temperature of ice}}.$$

If it be agreed to call the temperature interval between ice and steam on this scale 100° , the ratio will become

$$\frac{Q_1}{Q_2} = \frac{T + 100}{T},$$

where T is the absolute (thermodynamic) temperature of ice. To find the figure representing T in thermodynamic degrees, the value of the ratio $\frac{Q_1}{Q_2}$ must be determined. It can be shown, by methods which do not come within the scope of the present treatise, that if a perfect gas be used as the working substance in Carnot's engine, working between the boiling-point and freezing-point of water, the value of the ratio $\frac{Q_1}{Q_2} = \frac{373}{273}$ (nearly) and hence $\frac{T + 100}{T} = \frac{373}{273}$, and T , the temperature of melting ice, is 273 thermodynamic degrees. Hence the thermodynamic scale is practically identical with the gas scale, the deviation being very small when hydrogen gas is used as the thermometric substance. Accurately, absolute zero on the thermodynamic scale is -273.13° ; and this would be identical with the Centigrade scale if a perfect gas were available for constructing a gas thermometer. For most purposes it is sufficiently accurate to assume equality between the hydrogen and thermodynamic scales.

In terms of temperature, therefore, the efficiency of a reversible engine is given by the expression

$$\frac{T_1 - T_2}{T_1}$$

where T_1 is the absolute temperature at which heat is received, and

T_2 the absolute temperature at which heat is rejected. This follows from the equality

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

whence

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}.$$

Examples will now be given in which the efficiency formula thus derived is utilised.

Example 1.—To find the efficiency of a perfect engine which takes in heat at 200°C. , and rejects it at 110°C.

From the formula

$$\frac{T_1 - T_2}{T_1}$$

the efficiency is

$$\frac{473 - 383}{473} = \frac{90}{473} = \cdot 19$$

or 19 per cent.

Example 2.—To find the temperature at which a perfect engine must take in heat in order to possess an efficiency of $\cdot 25$, or 25 per cent. when heat is rejected at 80°C.

$$\cdot 25 = \frac{T_1 - T_2}{T_1} = \frac{T_1 - (273 + 80)}{T_1}$$

\therefore

$$\cdot 75T_1 = 353$$

and $T_1 = 470\cdot 7^\circ$ (absolute) or $197\cdot 7^\circ \text{C.}$

Example 3.—To compare the efficiencies of two engines, one working between 300°C. and 200°C. , and the other between 200°C. and 100°C.

The respective efficiencies are $\frac{573 - 473}{573}$ and $\frac{473 - 373}{473}$,

or 17·5 and 21·2 per cent.

Note that the difference between the working temperatures is the same in each case, viz. 100°C. , but as the quantity of heat taken in in the second case is less, the efficiency is greater than that of the first engine.

Energy Ratio of a Refrigerating Machine in Relation to Temperatures.—Taken with respect to the energy received and rejected, the ratio in the case of a refrigerating machine, working on a reversible cycle, has been shown to be

$$\frac{Q_2}{Q_1 - Q_2}$$

where Q_2 is the energy received from the evaporator coils, and Q_1 the energy rejected in the condenser. Hence, as $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$, the energy ratio in terms of temperature is

$$\frac{T_2}{T_1 - T_2}$$

the temperatures being in absolute degrees. Examples of the use of this formula are given in Chapter XVI.

Entropy.—A substance undergoing an isothermal compression or expansion alters in volume and pressure, but the temperature remains constant. Hence, if A, B and C (Fig. 106) represent the isothermals of a given mass of a substance, they may be distinguished from each other by reference to the existing temperature. Thus A might be the isothermal for 10° , B for 20° , and C for 30° , thus furnishing a constant distinction. If now we take the adiabatics $d f h$, $e g k$, cutting these isothermals, a constant distinction may be found between these also. As volume, pressure and temperature all alter during an adiabatic change, the constant difference referred to must relate to some other fundamental property of the substance, or be derived from two or more of the three properties named.

The characteristic feature of an adiabatic process is that heat is not permitted either to enter or leave the substance, whereas in an isothermal operation heat is allowed to enter or escape in such quantity as to prevent an alteration of temperature. If now we consider the cycle of operations in a Carnot's engine, represented by two isothermals and two adiabatics, such as $d e$, $f g$, and $d f$, $e g$ (Fig. 106) a quantity of heat Q_1 is taken in during the isothermal expansion $d e$ at a temperature T_1 (absolute), and a quantity Q_2 is rejected during the isothermal compression $g f$ at a temperature T_2 (absolute). The relation existing between these quantities has been shown to be

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}, \text{ and hence } \frac{Q_1}{T_1} = \frac{Q_2}{T_2}.$$

Similarly, $f g k h$ might represent the cycle of the engine when heat enters at T_2 , and is rejected in the isothermal compression $k h$ at a temperature T_3 , when as before $\frac{Q_2}{T_2} = \frac{Q_3}{T_3}$. Accordingly, any number of isothermals might be drawn intersecting the adiabatics $d f h$, $e g k$, and in each case the quantity of heat taken in (or given out), divided by the absolute temperature corresponding to the isothermals —that is $\frac{Q}{T}$ —would have the same value for the portions $d e$, $f g$, $h k$,

etc., bounded by the two adiabatics. Hence the substance, when taken through the adiabatic process egk , differs in condition from that which obtains for the process dfh by a constant value represented by $\frac{Q}{T}$. The difference of condition thus expressed is termed "*difference of entropy.*" During an isothermal expansion, such as de , heat enters

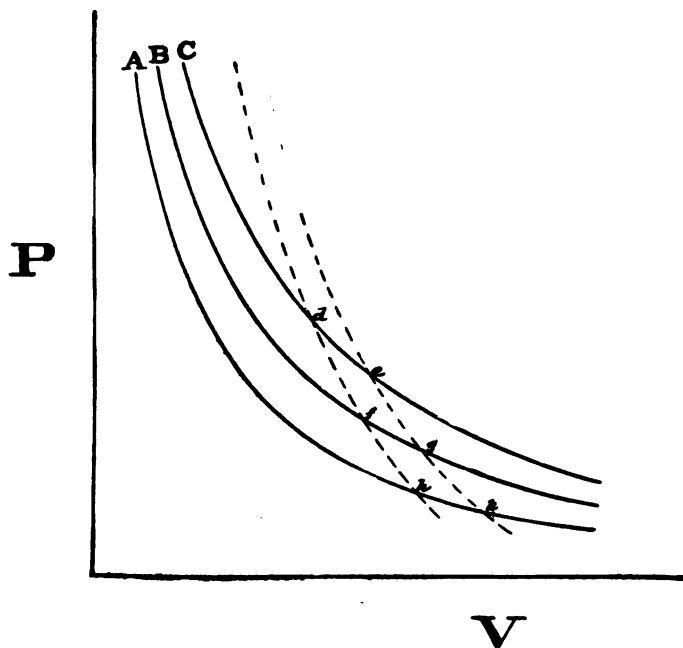


FIG. 106.—ISOTHERMS AND ADIABATICS.

the substance; and the difference in condition between e and d is expressed by saying that the substance has undergone an increase of entropy represented by $\frac{Q_1}{T_1}$; whereas in the isothermal compression gf heat escapes, and the substance suffers a decrease of entropy expressed by $\frac{Q_2}{T_2} = \frac{Q_1}{T_1}$. Hence the increase in the former equals the decrease in the latter, and the condition of the substance at d , from this standpoint, is identical with that at f or any other part of the adiabatic dfk . Evidently, therefore, a substance passing through an adiabatic change possesses a definite thermal property or condition which remains constant, and differs from the constant property exist-

ing in another adiabatic operation by the relation $\frac{Q}{T}$. To this constant thermal property the name of "entropy" is given. Although, at first sight, this property might appear to be a mere abstraction, it will be found on reflection to rank with the ordinary properties of matter, such as density and thermal capacity.

The zero of entropy, for convenience, is taken to correspond to the condition of water at 0°C . This zero, like that of the thermometric scales, is arbitrary, but serves as a starting point for entropy calculations. The entropy of a substance is usually signified by the letter ϕ , and much useful information may be gained from diagrams obtained by plotting entropy (ϕ) against absolute temperature, which in this connection is generally signified by the letter θ . Fig. 107, which represents the temperature-entropy

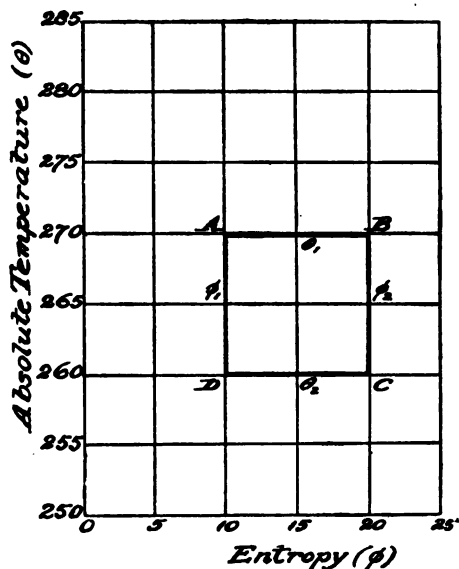


FIG. 107.—TEMPERATURE-ENTROPY DIAGRAM OF CARNOT'S ENGINE.

diagram of Carnot's cycle, will serve to indicate the usefulness of this method of representation. Assuming that 2700 units of heat are taken in at the higher temperature θ_1 , which is taken as 270° (abs.), the increase of entropy will be $\frac{2700}{270} = 10$ units. Taking A as the starting-point of the diagram, the line AB is drawn equal

to 10 entropy units on the scale chosen along the horizontal line through 270° , and represents the isothermal expansion in Carnot's cycle. The succeeding adiabatic expansion, during which the temperature falls from 270° to that of the cold body—here taken as 260° —is represented by the vertical line BC, as the entropy is constant during an adiabatic change. In the isothermal compression which follows, heat leaves the substance, going into the cold body; hence the entropy falls by an amount $\frac{Q_2}{\theta_2} = \frac{Q_1}{\theta_1} = \frac{2700}{270} = 10$ units.

Hence the line CD, 10 units long, drawn along the horizontal through 260° , represents the third operation. Finally, in the adiabatic compression, the temperature rises to 270° , whilst the entropy remains the same. Hence the figure ABCD represents the $\theta\phi$ diagram of an engine working on Carnot's cycle. The work done during the cycle is $J(Q_1 - Q_2)$. But the difference of entropy between the two adiabatics $(\phi_2 - \phi_1) = \frac{Q_1}{\theta_1} = \frac{Q_2}{\theta_2}$. Hence $Q_1 = \theta_1(\phi_2 - \phi_1)$; and $Q_2 = \theta_2(\phi_2 - \phi_1)$.

$$\text{Hence} \quad (Q_1 - Q_2) = (\theta_1 - \theta_2)(\phi_2 - \phi_1)$$

and the work done during the cycle is $J \times (\theta_1 - \theta_2)(\phi_2 - \phi_1) = J \times \text{area of square ABCD} = 100 J$. If the 2700 heat units assumed to enter be taken as calories, the work done will be $(100 \times 42,750)$ cm.-grms.; if B.Th.U., the work becomes (100×778) ft.-lb. This result agrees with that obtained from the efficiency formula $\frac{T_1 - T_2}{T_1} = \frac{10}{270}$; that is, $\frac{10}{270}$ of the total energy provided will be converted into work. As the work provided is 2700 J, the portion utilised as work is $\frac{10}{270} \times 2700 J = 100 J$.

The temperature-entropy diagram for 1 lb. of water or other substance may be constructed as follows. Let the entropy at 0° be called 0. Then on raising the temperature to 1°C. , the heat entering is 1 lb.-C. unit, and the average temperature at which this heat enters is 273.5° absolute. Hence the entropy of 1 lb. of water at 1°C. is $\frac{1}{273.5} = .003656$. If the temperature be now raised to 2°C. , the entropy will increase by $\frac{1}{274.5} = .003643$; and consequently the entropy of 1 lb. of water at 2°C. will be $(.003656 + .003643) = .007299$. In this manner the entropy corresponding to each degree can be calculated, and a $\theta\phi$ diagram constructed

from the figures. The entropy of 1 lb. of water at any temperature T (abs.) is given by the formula

$$\phi = 2.30 (\log_{10} T - \log_{10} 273).$$

In obtaining the diagram for saturated steam, it is necessary to take into account the latent heat of vaporisation, which enters without change of temperature. If, for example, the entropy of saturated steam at 175° C. be required (water at 0° C. being taken as 0), the entropy of water at 175° must be added to the increase of entropy which occurs during the change of state. The entropy of 1 lb. of water at 175° is 0.5; and the latent heat of 1 lb. of steam at 175° C. is 482.7 lb.-°C. units. The increase of entropy due to change of state is therefore $\frac{482.7}{(175 + 273)} = 1.08$; and hence the entropy of 1 lb. of steam at 175° is $(1.08 + 0.5) = 1.58$.

Temperature-entropy diagrams are frequently of service in elucidating problems arising in connection with the working of heat engines and refrigerating machines.

CHAPTER XXI.

THE CONVERSION OF HEAT INTO WORK. PRACTICAL
HEAT ENGINES.

General Remarks.—In the foregoing chapter the principles of thermodynamics have been considered in relation to an ideal engine, which cannot in practice be realised. The performance of any existing engine must of necessity fall short of the ideal, as losses must occur owing to the friction of parts, the escape of heat by radiation, and other causes. The main principles established, however, are applicable to all engines, and serve to show not only the limitations of any appliance for converting heat into work continuously, but also the best possible way in which such conversion could ever be conducted. The engineer must choose, from the fuels and materials at his disposal, those which can be utilised in such a manner as to produce the greatest amount of work at the minimum of cost; and although in doing this deviations may be made from what would appear to be the correct procedure theoretically, yet he must ever be guided in the main by the fundamental laws of thermodynamics. The extent to which actual engines may be made to approach the ideal, and the application of thermodynamic principles to problems connected with actual engines will form the substance of the present chapter.

Disposal of Heat in a Steam Engine.—As a starting-point for the consideration of the conversion of heat into work with practical appliances, the results of the trials made with a steam engine, fitted with all the modern apparatus available for securing economic working, will first be given. The engine under test was a Louisville-Leavitt pumping engine, and the figures given are taken from the Report of the Committee on the Thermal Efficiency of Steam Engines, published by the Institution of Civil Engineers in 1898. The heat entering or leaving each portion is given separately.

The most striking fact exhibited by the figures is that only a small proportion of the heat generated is converted into work, viz. 27,260 out of 183,600 B.Th.U. furnished by the fuel, or 14·85 per

DISPOSAL OF HEAT IN A STEAM-ENGINE PLANT.

	<i>Fire-grate.</i>	B.Th.U. per minute
Heat generated		183,600
Lost by radiation		10,000
Entering flue gases		41,900
Heat entering boiler directly	$(183,600 - 51,900) =$	131,700

	<i>Flue.</i>	
Total heat entering		41,900
Taken up by economiser (afterwards returned to boiler)		15,750
Radiation losses on the way to, and in economiser		6,000
Heat escaping up the chimney	$(41,900 - 21,750) =$	20,150

	<i>Boiler.</i>	
Received directly from firegrate		131,700
„ from economiser		15,750
„ from feed-water		5,450
„ from jackets		6,600
Less radiation losses in connections of economiser, etc.		250
Total Heat received by boiler		159,250

	<i>Cylinders.</i>	
Total heat leaving boiler		159,250
Radiation loss from connecting pipes, etc.		3,100
Heat entering cylinders		156,150
Utilised as work		27,260
Entering condenser		117,640
„ jackets		6,750
Radiation from engine		4,500
Temperature of entering steam		359° F.
„ escaping steam		100° F.

	<i>Condenser.</i>	
Total heat entering		117,640
Removed by cooling-water		110,240
Leaving in feed-water		5,700
Lost by radiation		1,700

	<i>Feed-Water.</i>	
Received from condenser		5,700
Radiation loss in connections to boiler		250
Entering boiler		5,450

	<i>Jacket-Water.</i>	
Heat entering from cylinders		6,750
Loss in connections to boiler		150
Returned to boiler		6,600

cent. A portion of the loss is due to the boiler ; but even if the engine itself be taken, the ratio of heat converted into work to that entering the cylinders is $\frac{27260}{156150}$; or deducting from the heat received the quantity returned to the boiler by the jacket and feed-water, the ratio becomes $\frac{27260}{142150}$, or 19·2 per cent. Even if radiation losses, and other means of escape of heat due to imperfect materials or appliances, could be entirely obviated, 104,200 B.Th.U. would still be required in the fire-grate to convert the same quantity as before—27,260—into work, or the ideal steam-plant would only possess an efficiency of 26·2 per cent. If, as in the previous case, only that portion of the heat which reaches the cylinders—less the quantity returned by the feed-water—be taken as the heat received, the efficiency of the idealised engine becomes $\frac{27260}{95300} = 28·6$ per cent.

Before proceeding to discuss the losses in detail, other methods of expressing the performance of this and other engines will be noticed. The indicated horse-power (I.H.P.) of the engine was 643, and the net heat supplied per minute 142,150 B.Th.U. Hence

$$\text{heat supplied per I.H.P. per minute} = \frac{142150}{643} = 221 \text{ B.Th.U.}$$

The brake horse-power of the engine was 599, therefore

$$\text{heat supplied per B.H.P. per minute} = \frac{142150}{599} = 237 \text{ B.Th.U.}$$

Both the above are useful methods of stating the thermal economy of an engine. The actual economy of the plant as a whole, however, is expressed by

$$\frac{\text{actual output of work}}{\text{work equivalent of heat of fuel}} = \frac{\text{brake horse-power} \times t}{(\text{heat produced by fuel in time } t) \times J}$$

The sources of loss will now be considered separately, and the extent to which each may be avoided or minimised discussed.

Radiation Losses from Steam-Pipe and other Surfaces.—Radiation from hot surfaces can never be prevented completely, but can be reduced to a minimum by the use of good lagging. The extent of the saving thus effected has already been indicated in Chapter XVII. Some heat will escape, no matter how well the hot surfaces are lagged, and beyond a certain thickness the lagging material costs more than

it saves. Direct radiation from the firebars into the ash-pit cannot be avoided; and the radiant heat escaping from the brickwork of the flue is also a source of unavoidable loss, which might, however, be minimised, if bricks of higher insulating power could be obtained. On the whole, there is practically no prospect of radiation losses being minimised to any greater extent than at present. In the plant under notice the total radiation losses amounted to 25,950 B.Th.U. per minute, or 14·1 per cent. of the total heat yielded by the fuel.

Flue-Gas Losses.—In order that combustion may be maintained in the furnace, it is necessary to create a sufficient draught in the chimney, to provide which the gases resulting from the combustion must be allowed to escape at a higher temperature than that of the atmosphere. Hence the loss of a quantity of heat in the flue-gases is unavoidable. Usually, in actual working, the loss on this account is in excess of the amount required to create the draught, and hence a saving is effected by allowing the hot gases, before escaping, to play on a series of pipes which contain feed-water for the boiler, the arrangement being known as an “economiser.” Allowing for this saving, the heat escaping into the chimney in the test described was 20,150 B.Th.U. per minute, or 10·9 per cent. of the total heat of the fuel. It would be difficult to minimise this loss under normal working conditions.

Condenser Losses.—By far the greater portion of the heat of the fuel—amounting in the present case to 110,240 B.Th.U. per minute, or 60·1 per cent. of the whole—escapes by the condenser, and is lost to the plant. It is essential that the entering steam, after performing its work, shall escape in the form of vapour; and hence the large quantity of heat required to convert the water in the boiler into steam is inevitably lost. By keeping the condenser as cool as possible the steam may be made to work expansively to a pressure equal to, or below that of the atmosphere, but the latent heat of vaporisation, given out when the steam condenses, is carried away by the cooling-water. A small fraction only is returned to the boiler in the feed-water derived from the condensation, which is warmer than water at atmospheric temperature. When a condenser is not used, the escaping steam may be employed to warm up the feed-water for the boiler, the arrangement for this purpose being termed a “feed-water heater.” In this case also only a small portion of the heat is saved, as every pound of escaping steam is replaced by 1 pound of feed-water; and at the best the heat utilised from each pound of steam is that required to raise 1 lb. of water from atmospheric temperature to the boiling-point. Thus if the escaping steam

be at 100°C. or 212°F. , the heat evolved by the condensation of 1 lb. would be capable of raising the temperature of $\frac{537}{90} = 5.97$, or nearly 6 lb. of water from 10°C. to 100°C. , or 50°F. to 212°F. ; whereas only 1 lb. of water is required to replace 1 lb. of steam. Hence in a feed-water heater utilising the heat of condensation in this manner, a waste of $\frac{5}{8}$ ths of the total is unavoidable. Any apparent superiority over a condenser in this respect is nullified by the fact that in a condensing engine more work is taken out of the steam before it is permitted to escape.

Working in the usual manner, there appears no possibility of minimising the condenser losses. Whether a saving can be effected by radical alterations in the plant, or by using some medium other than steam, will be considered subsequently.

Frictional Losses.—After deducting the various losses enumerated, only 27,260 B.Th.U. per minute, or 14.9 per cent. of the heat of the fuel, remain to represent the thermal efficiency, or proportion of the total heat converted into work in the cylinders. The whole of this however, is not available for external work, as some is lost in the friction of the moving parts of the engine, which causes a waste equivalent to 1870 B.Th.U. per minute. Hence the external useful work is represented by 25,390 B.Th.U. per minute, or 599 horsepower. The indicated horse-power would be the equivalent of 27,260 B.Th.U. per minute, or 643. The frictional losses might be minimised if ball-bearings could be employed throughout, but this is not feasible in practice, and hence the loss on this account is unavoidable also.

In the steam plant under notice, therefore, which possesses no obvious defects, and when worked with the utmost care, it is impossible to obtain a better output from 183,600 B.Th.U. per minute than 599 H.P., or 13.83 per cent. of the energy supplied. This proportion is so small that it is desirable to discuss the possibilities of increasing the efficiency of such an engine, either by a different method of procedure or other alterations. The points arising in this connection will now be noticed.

Availability of Heat.—After putting aside the radiation and frictional losses in a steam engine as incurable, owing to the imperfection of the materials at our disposal, the question of the utilisation of the heat lost in the condenser remains for consideration. Although the heat entering the condenser is great in quantity, it is useless to the engine, from a work standpoint, owing to the low temperature existing in the condenser. The second law of thermodynamics expresses

the impossibility of continuously performing work by transferring heat from the condenser to the boiler; and hence the usefulness of heat, in respect to its capability of being converted into work, depends upon temperature. The heat possessed by a body may be very great in quantity, but unless the body is at a sufficiently high temperature the heat is not available for the production of work.

The proportion of heat which may be converted into work in an ideal engine has been shown to be $\frac{T_1 - T_2}{T_1}$, and hence, unless heat is furnished at a higher temperature than that of the condenser (T_2), no work can be obtained from it. The availability of heat, therefore, is dependent on the absolute temperature, and not on the quantity. For example, to convert 1 lb. of water at 0°C . into steam at 120°C . requires 643 lb.- $^\circ\text{C}$. units, and to raise the temperature of 1 lb. of air from 0°C . to 3800°C . (at constant volume) requires 643 lb.- $^\circ\text{C}$. units also. A perfect engine taking in steam at 120°C . and rejecting it at 100°C . would possess an efficiency of $\frac{393 - 373}{393} = .051$ or 5 per cent. only; whereas if an engine could take in a gas at 3800°C ., and reject it at 100°C ., its efficiency would be $\frac{4073 - 373}{4073} = .91$ or 91 per cent., although the heat quantity involved is the same as in the case of the steam. It is evident, therefore, that the higher the entering temperature, and the lower the temperature of exit, the greater will be the proportion of heat energy available for producing work.

The increase of the temperature, in the case of steam, cannot be continued beyond the point at which the resulting pressure becomes too high to enable tight joints to be made, as the resultant leakage would counterbalance the advantage gained. In addition, the boiler and working parts would have to be made stronger, thus increasing the prime cost. Hence, however desirable from the standpoint of increased efficiency, a limit to working at high temperatures with steam is soon reached owing to mechanical considerations. At 200°C ., for example, the pressure of saturated steam is 225 lb. (absolute) per square inch, and small successive rises in temperature beyond 200° produce a constantly increasing rise in pressure. There is little chance, therefore, of increasing the upper temperature of the steam beyond the limits at present in use, with the present methods of construction of the engine.

The custom of superheating the steam before admission to the cylinder results in economy, chiefly from the fact that condensation in the passages and cylinder is largely prevented. At first sight it

might appear that by taking steam at—say— 150°C. , and superheating it to 200°C. , the advantage of working at a considerably higher temperature would result in a large increase of efficiency, compared with that obtained by working at 150° with saturated steam. The superheated steam, however, is essentially a different medium to saturated steam, and the efficiency formula $\frac{T_1 - T_2}{T_1}$

does not apply to a case in which the medium is changed during the cycle. Saturated steam at 150°C. has a pressure of 69.5 lb. (absolute) per square inch, and if heated out of contact with the water in the boiler the pressure rises in practically the same ratio as in the case of a gas. Calculated in this way, the pressure of the

superheated steam at 200°C. would be $69.5 \times \frac{(273 + 200)}{(273 + 150)} = 77.5$ lb. per square inch ; whereas saturated steam at 200°C. has a pressure of 225 lb., or nearly three times as great, and is evidently capable of performing far more work than steam which has been generated at 150° and superheated to 200° . Or, to view the question from another standpoint, the heat taken up by 1 lb. of steam when superheated from 150° to 200° will be the product

(weight \times specific heat \times rise in temperature)

or $(1 \times .48 \times 50) = 24$ lb.- $^{\circ}\text{C.}$ units. After admission to the cylinder, each pound of steam admitted will do work equivalent to 24 lb.- $^{\circ}\text{C.}$ units in cooling to 150°C. , after which the work performed will be that due to saturated steam cooling from 150° to the temperature of the condenser. If, instead of superheating, the steam in the boiler were heated to 200°C. , a far greater quantity of work would be performed owing to the superior pressure of the saturated steam. Hence the work-producing power of steam generated at a low temperature and superheated to a higher, should not be confused with that of saturated steam at the higher temperature ; nor must it be imagined that the efficiency of an engine using superheated steam can be expressed in terms of the temperatures of superheat and rejection, as the character of the medium changes fundamentally during the cycle. The chief advantages of superheating are due to the possibility of raising the temperature of the steam without greatly increasing its pressure ; the heat necessary for this process being afterwards converted into work, and the resultant steam rendered unsaturated and therefore not liable to condense. The limit of superheating is reached when the temperature of the steam is such that the materials of the cylinder are corroded.

The extent to which the temperature of the condenser may be lowered is restricted in practice by the supply and temperature of the cooling-water. In the steam-test previously described, the condenser was kept at 100°F. (38°C.), and to secure so low a temperature as this entails the use of a most efficient condenser and a plentiful supply of cold water. Sulphur dioxide in the liquid form, which may be produced by little expenditure of energy from the gas, has been used in Germany to maintain a lower condenser temperature than is possible with water-cooling. In the best case, however, a limit would be reached at 32°F. or 0°C. , at which temperature the water would freeze. Hence, owing to practical difficulties, the availability of energy imparted to steam is restricted by an upper temperature limit lying between 200°C. and 300°C. , and a lower limit of 32°F. or 0°C. Any improvement on existing steam-engines, in respect to efficiency, will be such as to permit of a greater range of working temperatures by raising the upper limit, or which reduce losses at present unavoidable.

Mention may be made here of the use of exhaust steam from a non-condensing engine for the purpose of working a second or supplementary engine, in which the medium is a more volatile liquid than water. Ether, for example, boils at 35°C. , and at 90°C. exerts in a closed space a pressure of 70 lb. per square inch (abs.). Exhaust steam might thus be used to heat a boiler containing ether, and an engine might be driven by the ether vapour. This method has occasionally been tried, but although a considerable saving of heat results, the cost of the engine and its upkeep are such as to reduce in a large measure the net financial saving; and from this standpoint a feed-water heater is generally preferred. Methylated spirits has been used as the medium for these supplementary engines.

Steam compared with other Media.—In an ideal engine, working between limits of temperature T_1 and T_2 , the efficiency would be the same, no matter what medium were used. It does not follow, however, that all media would be equally suitable in practice. If steam and air be compared as media, working between limits of 200°C. (473°abs.) and 40°C. (313°abs.), there would be no choice so far as the proportion of heat converted into work was concerned. Saturated steam at 200°C. , however, has a pressure of 225 lb. per square inch (abs.), whereas air, taken as being at atmospheric pressure at 40°C. , would only possess a pressure of 22.2 lb. (abs.). It is evident, therefore, that in order to furnish the same horse-power the area of the piston of the air engine would have to be many times

as great as that of the steam engine, and this unwieldy size would not only entail greater prime cost, but also larger expenses in upkeep. Even if the temperature of the air were 1000°C ., the pressure would only be 60 lb. (abs.) per square inch, and if such a working temperature were possible the size of the engine would still be a fatal drawback. The use of gases is further discounted by the fact that the supply of hot gas from a boiler would be difficult to maintain; whereas water represents concentrated steam, 1 cubic inch producing nearly a cubic foot of steam. Hence, using a boiler, practical difficulties prevent the use of gases as a substitute for steam. The internal combustion engine, however, enables gases to be used to advantage, as will be shown later.

The vapours of other liquids, such as ether, alcohol, petroleum, etc., cannot be substituted for steam, for various reasons, and no advantage would accrue from their use unless they could be made to work between wider limits of temperature than steam. All these liquids are costly compared with water, and the three named are highly inflammable, so that a leakage would be a source of danger. Water, by its abundance, non-inflammability, and comparatively small chemical action on metals, is preferable to any other liquid at present known; and to justify the substitution of another liquid it would be necessary that such liquid should possess, in large degree, the advantages enumerated, and should be capable in addition of being worked between wider limits of temperature than water, so as to procure an increase of efficiency.

Cycle of Operations in a Steam Engine.—It now remains to be considered whether it is practically possible to modify the cycle of operations in a steam engine so as to secure a greater efficiency. Referring to the indicator diagram (Fig. 108) the nearly vertical

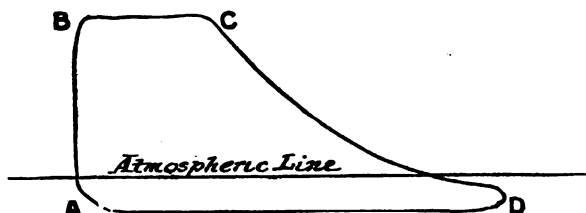


FIG. 108.—INDICATOR DIAGRAM OF CONDENSING STEAM ENGINE.

line A B represents the rise of pressure due to the admission of steam to the cylinder. Whilst the valve remains open, this pressure will remain constant, as shown by the line B C, which represents the

isothermal of saturated steam at the boiler temperature, and is therefore horizontal. The curved line CD represents the fall of pressure due to the work done by the expansion of the steam, and is approximately an adiabatic, not quite fulfilling this condition owing to the escape of heat through the walls of the cylinder. At D the cylinder is made to communicate with the condenser, and the piston moving backward drives out the steam at the pressure and temperature existing in the condenser. Hence the line DA is the isothermal of water vapour at the temperature of the condenser, and is horizontal. The area of the closed figure ABCD represents the work done during the cycle, when the units taken correspond to the actual volume of the cylinder, and the actual pressures.

An important difference between this cycle and that of Carnot's engine is at once apparent. Whereas, in an ideal engine, the working substance remains in the cylinder and is not renewed, the steam after expanding is expelled, and replaced by fresh steam. If it were possible to compress and re-heat the expanded steam *in situ*, a boiler would no longer be necessary. No arrangement has yet been devised, however, which would make such operations possible, and even if such arrangement were forthcoming, it would suffer from similar heat losses by radiation, etc., as the boiler itself. Moreover, in compressing the expanded steam isothermally, condensation would ensue, and the water produced would have to be converted into steam again by the heat applied to the cylinder. The rapid application of heat to the cylinder at one part of the stroke, and the almost instantaneous extraction of heat which would be requisite at another part, are not practically possible; and hence the replacement of the working substance once per cycle is a necessity in the steam engine and also in internal combustion engines. Comparing the indicator diagram under notice with that of Carnot's engine on page 388, the line BC is the equivalent of the isothermal DA (although different in shape), the boiler being analogous to the hot body. The line CD is similarly equivalent to the adiabatic AB, work being done in both cases by the expanding medium, which falls in temperature. Here the resemblance ceases, as no attempt is made in the steam engine, for the reasons stated, to bring the steam back to its original hot state by means of processes analogous to the isothermal and adiabatic compressions BC, CD. Any improvement in efficiency which might result from the alteration of the existing cycle so as to make it reversible, must be regarded as unattainable in practice.

Conclusions Regarding Steam Engines.—In the foregoing pages it

has been shown that the low efficiency of steam engines arises from a variety of causes, and future improvements in this respect will depend upon the introduction of higher working pressures (and temperatures) and lower condenser temperatures, and in such minor savings as the lessening of radiation and condensation. Viewed from the standpoint of thermal efficiency, steam engines are greatly inferior to internal combustion engines, as will appear subsequently. Until quite recently, however, it has been found more economical to use steam engines for most purposes, as the inferior efficiency was more than counterbalanced by the cheapness of coal compared with gas. Since the introduction of cheap producer gas, however, this advantage on the part of the steam engine has ceased to exist, with the result that steam power has been in many cases supplanted by the cheaper gas power, particularly for generating horse-powers below 100. For power production on the largest scale, however, the steam engine possesses the advantage in respect to size, and where space is a consideration this fact is of importance. It cannot be predicted at present as to what is the upper practicable limit of power production by the internal combustion engine, but plant of 3000 H.P. has already been laid down. The reciprocating steam engine is reversible in direction, whereas the internal combustion engine is not; and this reversibility is essential in many engines, such as locomotives. For high-speed working the steam turbine is the best engine yet introduced, the vibration caused by reciprocating engines being largely obviated. The conversion of heat into work in the steam turbine is essentially the same as in the reciprocating engine, the steam being admitted at high pressure and allowed to work expansively to a low pressure, the work being applied to the rotation of the shaft instead of the longitudinal movement of a piston. This is the latest form of the steam engine, and there does not appear any immediate prospect of the general replacement of steam power for very large-scale purposes by any other type of engine.

Disposal of Heat in Internal Combustion Engines.—By generating the heat in the cylinder of the engine itself, instead of employing an intermediary such as steam, the losses inseparable from the use of a boiler are avoided. In gas engines a mixture of combustible gases with air is exploded, the resultant chemical action giving rise to the heat; whilst in oil engines the vapour of the oil, mixed with air, is similarly used to produce heat. In each case work is done on the piston by the expansion of the hot gases resulting from the combustion.

As the explosion of the mixtures gives rise to a high temperature

—1500° C. or more—it is evident that unless steps are taken to keep the cylinder cool the engine could not be worked, as the charge would ignite immediately on entering. Hence a circulation of water must be kept up round the cylinder, to ensure that the walls are kept well below the temperature of ignition of the explosive mixture. In practical working, therefore, a portion of the heat generated must of necessity be carried away by the cooling-water, and in consequence is not available for conversion into work. A further loss is caused by radiation from exposed parts, although this is relatively small; and in addition the gases, after expanding, are expelled from the cylinder whilst still retaining a considerable portion of the heat generated. As the piston is urged forward against the pressure of the atmosphere, it is evident that the hot gases would cease to expand and do work when the pressure exerted was equal to that of the atmosphere, and in practice the expansion cannot be carried to this limit. Hence, in internal combustion engines, there are three unavoidable sources of heat loss in practice, viz. in the cooling-water, by radiation, and in the escape-gases.

In a well-designed internal combustion engine the disposal of heat is approximately as under :—

	Per cent.
Loss to cooling-water, and by radiation	25
Loss in escape gases	35
Converted into work	40

The thermal efficiency—40 per cent.—is therefore much higher than that obtainable with a steam engine, but whether any financial advantage is gained depends upon the relative costs of fuel, upkeep, and prime costs of the engines. All these points must be considered in deciding upon an engine to be used under given circumstances.

The “mechanical” efficiency, or proportion of heat available for external work, is less than the thermal efficiency owing to frictional losses in the engine itself. These losses amount to about 3 per cent. of the total heat provided; and hence the mechanical efficiency of a good internal combustion engine is about 37 per cent.

The superior efficiency of these engines over the steam engine arises from the fact that the operations take place between wider limits of temperature. The absence of boiler losses is counter-balanced by the loss to the cooling-water; and the greater efficiency results from the use of a higher working temperature, and consequent greater availability of the heat. The experimental difficulties of obtaining exact data relating to the working temperatures have not yet been overcome; but assuming the temperature produced by the

explosion to be 1500°C. , and that of the escape gases to be 500°C. , the efficiency of a perfect engine working between these temperatures would be $\frac{1773 - 773}{1773}$ or 56.5 per cent. Compared with this, a perfect engine taking in heat at 200°C. , and rejecting it at 60°C. (the temperatures that might exist in a steam engine working with a condenser) would have an efficiency of only 29.6 per cent.

It is evident that an increase in the temperature produced by the explosion, and a diminution of the temperature at which the hot gases are expelled, would raise the efficiency of an internal combustion engine. The possibility or advisability of modifying these temperatures is subject to practical limitations. The existence of a very high temperature on the inner surface of the cylinder, fluctuating at different parts of the cycle, and of a uniform low temperature on the exterior, subject the material to severe strains and stresses; and so far as the life of the engine is concerned, it is most economical to employ as low an explosion temperature as possible, and special means of reducing this temperature have been tried. The lowest temperature possible for escaping gases to possess would be that at which the pressure exerted would be equal to that of the atmosphere. To attain this temperature in practice it would be necessary to produce by the explosion just sufficient heat to enable the resulting gases to expand so as to fall to atmospheric pressure when the piston is at the end of its stroke. The difficulties arising in practice tend to make this desired end unattainable. The explosive mixture after ignition has a different composition to that possessed on entrance to the cylinder, and would occupy a different volume at the same temperature; and it would be necessary so to regulate the quantities of air and combustible matter drawn in that the resultant gases would just fill the cylinder at atmospheric pressure. Moreover, each explosion would have to be uniform in character—which is not always the case in practice—and hence the expansion of the gases down to atmospheric pressure cannot be ensured. The nearer this end is attained, by regulation of the charge and size of the combustion chamber, the greater will be the efficiency.

Cycle of Operations in Internal Combustion Engines.—Whereas in the steam engine the cycle is completed in one forward and one backward movement of the piston, all ordinary internal combustion engines require two complete forward and backward movements in passing through the cycle. The operations are as follows:—

1. *Backward Stroke.*—Charge of air and combustible gas or vapour enters cylinder.

2. *Forward Stroke*.—The mixture is compressed, and fired at or near the end of the stroke, causing a great increase in pressure.
3. *Backward Stroke*.—The hot gases expand, doing work on the piston, and consequently falling in temperature.
4. *Forward Stroke*.—The expanded gases are removed from the cylinder.

These operations are shown in the indicator diagram, Fig. 109. Starting at the point A, the charge is drawn in at atmospheric pressure, as indicated by the horizontal line A B. The next operation—compression of the charge

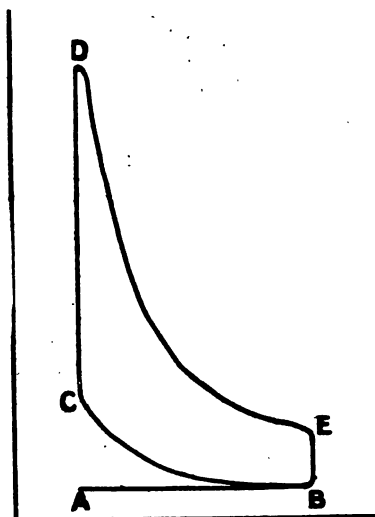


FIG. 109.—INDICATOR DIAGRAM OF INTERNAL COMBUSTION ENGINE.

—is shown by the curved line BC (approximately an adiabatic). The vertical line C D represents the rise of pressure due to the explosion of the charge; and D E—also approximately an adiabatic—the expansion of the hot gases during the second backward stroke. At E the exhaust opens, and the pressure falls to atmospheric, as shown by the vertical line E B. Finally, on the forward stroke which follows, the expanded gases are expelled at atmospheric pressure, as indicated by the line B A. The closed figure B C D E represents the work done during the cycle.

It will be noticed that this cycle, like that of the steam engine, is not reversible. Compared with Carnot's cycle, the adiabatic compression B C and the expansion D E correspond to C D and A B in Fig. 105. The heat is not taken in, however, from a body at constant temperature, but suddenly developed in the charge itself; and the isothermal compression in Carnot's engine (B C, Fig. 105) is also absent. Although falling short of the ideal cycle, however, the set of operations employed in internal combustion engines result in the utilisation of a relatively large proportion of the heat furnished by the explosion. Diagrams obtained in practice will differ from Fig. 109 according to the time at which the charge is fired; the rate of burning of the charge; and the amount of expansion permitted before the exhaust opens. Firing the charge before complete com-

pression enables the pressure to rise to a maximum by the time the compression stroke is completed, the combustion not being instantaneous; and in this case the line DC will be curved, the position of C depending upon the part of the stroke at which firing takes place. Further expansive working would prolong the line DE and shorten EB, evidently demanding a longer stroke.

Conclusions regarding Internal Combustion Engines.—Compared with the steam engine, internal combustion engines as a class are capable of yielding a much higher thermal efficiency. Whether an actual financial saving results from the use of the latter class depends upon the cost of the fuel. Where blast-furnace gases are available, an extremely cheap source of power is obtained for the driving of machinery connected with the works. Mond's gas, made from coal slack, is also very cheap; and suction gas taken directly into the engine is a further source of cheap fuel. In the vapour engines used for motor-cars, volatile fuels of the type of petrol, benzol and alcohol are used; which are relatively costly compared with gas or coal. In oil engines, however, in which the cheaper varieties of oil can be used—such as in the Diesel engine—the cost per horse-power is less than with steam. The following figures are given by Mr. Swinburne as representing the brake horse-power hours obtainable with the various types of engine and fuels, for an expenditure in each case of 100*l.*—this sum including the cost of labour, lubricants, cooling water, fuel, and any other details of upkeep :—

	B.H.P.	Hours per £100.
Gas engine using Mond's gas	235,000	
„ „ suction gas	202,500	
Diesel oil engine	181,000	
Steam plant (condensing)	72,500	
Explosion oil engine	68,500	
Gas engine with town gas	52,600	

As might be expected from the above figures, modern internal combustion engines are now formidable rivals to steam engines. The production of cheap gas has given a great impetus to the use of gas engines, and the tendency at the present time is to instal gas engines—or a good form of oil engine—in preference to steam plant, up to a certain horse-power. Large gas engines are now being introduced capable of producing 3000 H.P., on the multi-cylinder system; and single units of 1000 H.P. are in use. Such engines take up a larger space than steam engines of corresponding power; but where space is not an important consideration it is probable that steam will largely be superseded in the future, even for large-scale power production.

At present the use of steam for generating 100 H.P. or more is general, and for the highest horse-powers—such as those requisite in large steamers—no rival to steam has yet been found. It may be confidently predicted, however, that the internal combustion engine, owing to its superior economy, will have its applications continuously extended. The drawback of lack of reversibility in these engines applies also to the steam turbine, and may probably be overcome.

Refrigerating Machines.—As a refrigerating machine is engaged in extracting heat, the losses, from a refrigerating standpoint, are due to the ingress of heat from surroundings. Thus the tanks containing the brine receive heat from without, as also do the various pipes conveying the brine, and this results in a loss of efficiency. The same is true of a cold store or ice-making plant. As the difference between the atmospheric temperature and the cold parts is relatively small—say 40° C. in a temperate climate—the loss of efficiency is not of the same order of magnitude as that which obtains from similar causes in a heat engine. Friction of parts in the engine is a further source of loss; but if the condenser water become heated above atmospheric temperature, radiation from it into the air is a gain to the machine. Evidently the efficiency will be less in a hot climate, and a good result for a compression machine, working under favourable conditions would be represented by a practical energy ratio of 3. As each plant

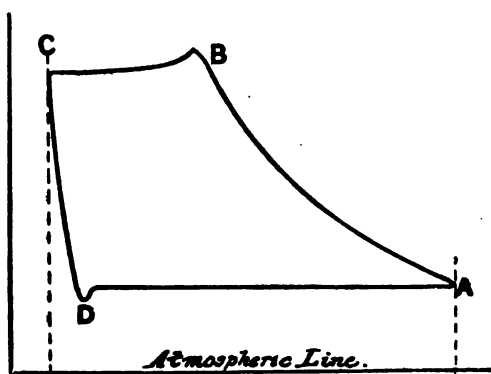


FIG. 110.—INDICATOR DIAGRAM OF REFRIGERATING MACHINE
(Compression System.)

varies so much in the detail of the refrigeration performed, it is difficult to procure general details of the losses, which in an average case amount to 50 per cent. of the heat-extracting power in the aggregate.

Cycle of Operations in a Refrigerating Machine.—Fig. 110 repre-

sents the general type of indicator diagram furnished by a compression machine. Starting at A, the gas is compressed adiabatically, as represented by the line A B. At B the valve opens, the prominence at this point being due to the lifting of the valve. The compressed gas now communicates with the condenser, which contains the liquid gas, and hence the pressure remains at that of the condenser for the rest of the stroke. This is shown by the horizontal part of B C, which is the isothermal of a vapour in contact with its own liquid. At C the piston commences the return stroke, and the pressure falls in the manner indicated by the adiabatic C D. At D the valve to the evaporator opens, causing the prominence at D, and the remainder of the stroke is accomplished at the pressure existing in the evaporator coils. As these contain the liquid, the line D A will be horizontal, and represents the isothermal of the saturated vapour at the temperature of the evaporator coils.

It will be observed that this cycle is bounded by two isothermals and two adiabatics, and is in reality a reversed Carnot's cycle. As such it is not susceptible of improvement, but in practice the compression A B and the expansion C D are not truly adiabatic. Other differences, such as fluctuations of pressure along B C and A D may also be noted frequently, but the cycle in general is such as to secure the best refrigerating effect from a given amount of work.

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